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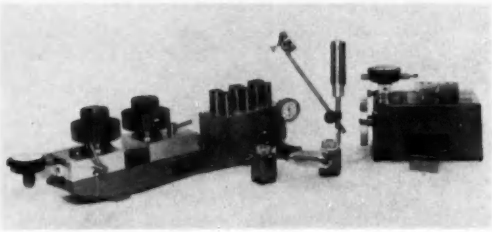

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VOL. XXIX *April 1959* NUMBER 4

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TEXTILE RESEARCH JOURNAL

PRINCETON, NEW JERSEY

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Dear Readers:

Since this is the last issue in which my name will appear as Editor of TEXTILE RESEARCH JOURNAL, I am taking advantage of this opportunity to express my sincere appreciation for the cordial relations that I have enjoyed with the many authors throughout the world whose papers have appeared in the JOURNAL, and to those persons who have so freely given of their time to painstaking reviews of papers submitted. I have a deep sense of obligation because whatever measure of success has been achieved by the JOURNAL has, I feel, been in large measure due to their efforts in its behalf.

To those readers who have not been aware of my pending retirement, I am officially giving up my position as Editor of the JOURNAL and Director of Publications of Textile Research Institute as of May 1, 1959, but continuing with the Institute as Consultant.

Dr. Richard K. Toner, Associate Professor in the Chemical Engineering Department of Princeton University, who has been acting as Assistant Editor of the JOURNAL since November 1, is taking over my duties. His knowledge of the sciences and experience in editing and writing make him fully qualified for the position.

It is gratifying to know that the JOURNAL will be in competent hands and that the established editorial policies will be maintained without change. I am also sure that Dr. Toner will be privileged to enjoy the same fine cooperation that I have had and that the JOURNAL will maintain its high standard of service to you and to industry.

Again let me thank all who have helped with the development of the JOURNAL. I should like to add that my seventeen years with the JOURNAL and with Textile Research Institute have been personally rewarding in many ways, not the least of which has been the personal friendships which I have been privileged to enjoy. I intend to continue some of my Association activities for a time, and my residence after July 15 will be Laureledge, Beech Haven, Athens, Georgia.

With warmest regards,

Sincerely,

Julian S. Jacobs

APRIL 1959
VOL. XXIX NO. 4

TEXTILE RESEARCH JOURNAL

Mechanical Behavior of Cyanoethylated Cotton Textiles[1]

Carl M. Conrad

Southern Regional Research Laboratory,[2] New Orleans, Louisiana

Abstract

A rather detailed study has been conducted at the Southern Regional Research Laboratory, as well as at other places, on the textile properties of cyanoethylated cotton. For the most part the studies have been concerned with improvements in rot and heat resistance and a comparison of such improvements with those resulting from acetylation of cotton. In the course of these studies various mechanical properties have been measured. These include breaking strength, knot strength, tearing strength, ultimate elongation, tensile and flexural stiffness, toughness, elastic recovery, wrinkle recovery, and flex and flat abrasion resistance. While many of these data have been published, they are in most cases reported incidentally and with little effort at completeness. The results are expressed in varying units, thus limiting their ready comparisons. Finally, they are widely dispersed in many papers, thus not readily accessible. It is the purpose of the present report to assemble the mechanical data on fibers, yarns, and fabrics; to express them in consistent units; and to interpret them in terms of degree of cyanoethyl substitution, conditions of reaction, textile products involved, and fine structure of the fiber. The report also points out the still unexplored areas of chemical substitution, textile product, and conditions of treatment which are in need of further study if an adequate picture of the mechanical behavior of cyanoethylated cotton is to be provided.

THE cyanoethylation of cotton textiles has been studied at the Southern Regional Research Laboratory, and at other places, to determine the effect of this chemical modification on rot and heat resistance and the relative merits of this treatment as compared with acetylation and other chemical modifications. In the course of this study, a very considerable amount of mechanical data has been collected and evaluated. Mechanical properties, as defined here, are those responsive to external forces "which tend to stretch, or compress, or bend or twist" as outlined and discussed, especially, by H. DeWitt Smith [31]. They include strength, elongation, stiffness, toughness, elasticity, resilience, and abrasion resistance in one or more forms. A number of these properties have been measured incidentally on partially

[1] Based on a paper presented at the Symposium on Mechanical Behavior of Heterogeneous Systems, San Francisco Meeting of the American Chemical Society, April 13–18, 1958.

[2] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

cyanoethylated cotton for a variety of utilization applications, but in few (if any) cases to characterize the mechanical properties as such. The pertinent data are, therefore, scattered through a number of publications, and are not readily accessible. Also, they are expressed in various systems of units and, for comparative considerations, they need to be expressed in comparable units. It is the purpose of the present paper to bring most of these data together, to adjust them where necessary to common units, and to record them in relationship to the degree of substitution of the cellulose (or some alternative unit), the conditions of reaction, and the characteristics of the textile used. In several cases previously unpublished data are presented.

Interest in the cyanoethylation of cellulose with acrylonitrile is indicated by patents [19] and subsequent reviews [2, 3, 4, 5, 24, 25]. Data on mechanical properties are incomplete to a considerable extent as to construction of textiles, conditions of reaction, and degrees of substitution. Figure 1 shows more clearly the present status.

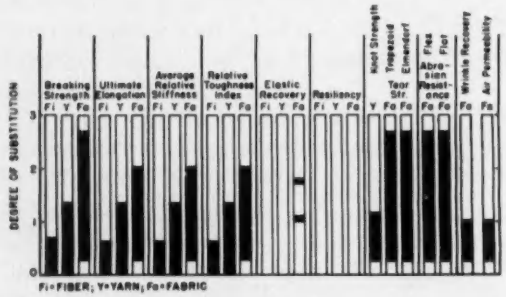

Fig. 1. Present status on study of mechanical properties of cyanoethylated cotton with reference to degrees of substitution. Shaded bars indicate some data available; open bars indicate lack of data.

The data abstracted from previous publications, generally recomputed, or previously unpublished data are presented in Tables I–XV.

Textile Materials and Methods Used

The textile materials discussed are limited to the following: (a) rovings—Rowden 41B [13]; (b) yarns—Deltapine 14/2 (42 × 2 tex) [16]; Rowden 41B, low twist, 16/2 (36.9 × 2 tex) [13, 14]; 40/2 (14.8 × 2 tex) and 60/2 (9.8 × 2 tex) [5]; sewing thread, 12/5 (49.2 × 5 tex) type used for commercial bags, both untreated and scoured [9, 14, 26]; (c) fabrics—fabric, 4-oz., from Wright Air Development Center [15]; duck, 8-oz. [5]; sheeting, 48 × 48 [14, 28]; print cloth, 80 × 80 [5, 14, 20].

Samples of roving, yarn, or sewing thread were treated by Daul and others [9], or by similar methods, usually in 20-yd. skeins. Their treatment consisted of first soaking the untreated or scoured material in 2% sodium hydroxide (in a few cases other concentrations were used, as indicated), centrifuging to 60–100% wet pick-up, immersing the sample in liquid acrylonitrile at a selected temperature, usually 55–60° C., for a variable time necessary to give the

TABLE I. Mechanical Properties of Control and Cyanoethylated Rowden 41B Cotton Fibers and Bundles*

Treatment	Substitution, degree	Estimated weight increase, %	Breaking load†		Ultimate elongation		Av .rel. stiffness, %	Relative toughness index, %
			Absolute, g.	Relative, %	Absolute, %	Relative, %		
			Fibers (7.8 mm. gauge)					
Untreated control	0	0	28.0	90	8.0	92	98	83
Pretreated control‡	0	0	31.0	100	8.7	100	100	100
Cyanoethylated**	0.36	11.5	27.4	88	7.3	84	105	74
Cyanoethylated**	.42	13.5	29.4	95	8.5	98	97	93
Cyanoethylated**	.61	20.0	25.5	82	7.2	83	99	68
			Bundles (2.5 mm. gauge)					
Pretreated control‡	0	0	20.2	100	6.56	100	100	100
Cyanoethylated**	0.34	11.1	19.7	98	6.00	92	106	90
Cyanoethylated**	.46	15.0	20.9	104	5.32	81	128	84
Cyanoethylated**	.70	22.9	21.1	105	6.16	94	112	99

* Computed from data of Grant [13].
† Adjusted to grams per tex of pretreated control.
‡ Padded with 2% NaOH, not reacted with acrylonitrile.
** Allowed to shrink during reaction.

desired degree of addition, washing, souring in 5% acetic acid, washing thoroughly, and drying at 105° C. Control samples were usually taken before any treatment and after alkali padding only.

In some of the later work the authors employed the reaction conditions outlined by Weaver, Klein, and others [21, 32]. These provide optimum ratios of water, cellulose, and alkali with large excess of acrylonitrile.

In special treatments, Haydel and others [16] used 40-yd. skeins (some specially prestretched), immersed them for 2 min. in 0.4% aqueous potassium persulfate solutions containing 0.1% wetting agent, centrifuged them to 80% wet pick-up, transferred them to a vapor phase reactor, evacuated, and treated them with acrylonitrile vapor at 80° C. for 10 min. This treatment did not give a cyanoethylated cellulose, but deposited polyacrylonitrile on and in the fibers. The unpolymerized acrylonitrile vapor was drawn off; the yarns were washed with water and dried in cool air. Suitable controls were retained.

Fabrics described by Daul [9] were usually re-

TABLE II. Mechanical Properties of Partially Cyanoethylated Doubled Cotton Yarns *

Designated yarn number, tex	Substitution, degree	Estimated weight increase, %	Breaking load†		Ultimate elongation		Av. rel. stiffness, %	Relative toughness index, %
			Absolute, g.	Relative, %	Absolute, %	Relative, %		
14.8 × 2	0	0	14.2	100	4.5	100	100	100
14.8 × 2	0.51	16.6	21.5	151	6.5	144	105	217
9.8 × 2	0	0	15.9	100	5.0	100	100	100
9.8 × 2	0.45	14.7	16.2	121	5.5	110	110	133

* Computed from data of Compton et al. [5].
† Adjusted to grams per tex of untreated control.

TABLE III. Mechanical Properties of 5-ply Sewing Threads and 2-ply Yarns as Related to Degree of Cyanoethylation *

Preparation	Substitution, degree	Estimated weight increase, %	Breaking load†		Ultimate elongation		Average relative stiffness, %	Relative toughness index, %	Relative knot strength, %
			Absolute, g.	Relative, %	Absolute, %	Relative, %			
Sewing thread, 12/5 (49.2 × 2 tex)									
None	0	0	18.19	120	8.9	82	146	98	104
Pretreated‡	0	0	15.10	100	10.8	100	100	100	100
Cyanoethylated	0.36	11.8	14.63	97	10.3	95	102	92	93
Cyanoethylated	.51	16.6	14.81	98	11.6	107	92	105	93
Cyanoethylated	.56	18.3	13.68	91	12.4	115	79	105	91
Cyanoethylated	.62	20.2	13.45	89	13.1	121	74	108	85
Cyanoethylated	.81	26.4	12.64	84	14.1	130	65	109	85
Scoured**	0	0	19.46	108	13.2	107	101	116	104
Pretreated‡	0	0	17.95	100	12.3	100	100	100	100
Cyanoethylated	.26	8.5	16.11	90	11.5	93	97	84	98
Cyanoethylated	.30	9.8	15.72	88	13.0	106	83	93	95
Cyanoethylated	.48	15.7	16.84	94	14.0	114	82	107	97
Cyanoethylated	.59	19.3	15.37	85	14.2	115	74	98	94
Cyanoethylated	.77	25.1	12.67	71	14.5	118	60	84	90
Yarn, 16/2 (36.9 × 2 tex)									
Pretreated‡	0	0	13.3	100	8.4	100	100	100	—
Cyanoethylated	0.36	11.8	15.4	116	8.4	100	116	116	—
Cyanoethylated	.42	12.9	17.6	132	8.5	101	131	133	—
Cyanoethylated	.61	18.7	16.5	124	9.0	107	116	133	—

* Computed from data of Grant et al. [13, 14].
† Expressed in grams per tex of unreacted control.
‡ Received padding with 2% NaOH only.
** Scoured with ethanolamine before reaction.

acted in a way similar to that employed for yarns and threads without tension.

Fiber and fiber bundle tests were made by McDonald and coworkers [23] on fibers prepared by defibering treated yarns or rovings. Yarns and threads in almost all cases were tested on a Scott IP-2[3] tester by standard ASTM [1] methods. Fabrics were sampled, and in most cases raveled to a fixed number of ends for tensile and elongation measurements. Flexural stiffness, tearing strength, flex and flat abrasion resistance, wrinkle recovery (crease resistance), and air permeability were all determined by ASTM methods [1]. Flat abrasion cycles were expressed in log units for comparison [30].

[3] The mention of trade names or manufacturers is not to be construed as a recommendation by the U. S. Department of Agriculture over equivalent products or other companies.

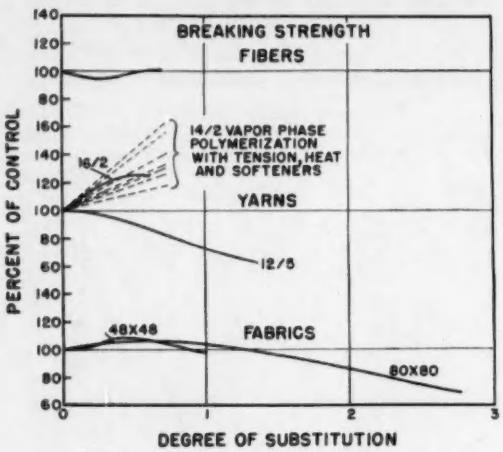

Fig. 2. Changes of breaking strength of fibers, yarns, and fabrics with degree of cyanoethylation.

Since alkali padding alone caused significant changes in a number of the mechanical properties, the basic control samples were pretreated with a suitable concentration of sodium hydroxide (2% or 10%), washed, soured, washed thoroughly, and allowed to dry.

Consideration of Experimental Data

Breaking Strength

In completely cyanoethylated cotton, the weight of the textile is essentially doubled over that of its unmodified control. For commercial purposes the added weight may be important. However, in the present discussion, in order to focus attention upon indirect tensile changes of the textile material resulting from chemical modification, results are expressed in terms of breaking load.

The strength of Rowden 41B cotton fibers, as measured on single fibers and on bundles, was little

TABLE IV. Mechanical Properties of 14/2 (42 × 2 Tex) Cotton Yarns Coated with Polyacrylonitrile under Various Conditions *

Treatment	Estimated weight increase,† %	Breaking load		Ultimate elongation		Average relative stiffness, %	Relative toughness index, %
		Abs., g.	Rel., %	Abs., %	Rel., %		
Controls:							
Scoured	0	1060	100	9.5	100	100	100
Dry stretched	0	1113	105	5.1	54	194	57
Wet stretched	0	1110	105	4.3	45	233	47
Vapor reacted:							
Unstretched	23.5	1334	126	7.4	78	162	98
Dry stretched	23.5	1485	140	6.1	64	219	90
Wet stretched	23.5	1651	156	5.4	57	274	89
With tension‡	23.5	1713	162	3.0	32	506	52
After stretched**	23.5	1410	133	6.7	71	187	94
Same, tempered††	23.5	1385	131	4.4	46	285	60
Same, softened‡‡	23.5	1245	118	5.7	60	197	71

* Computed from data of Haydel et al. [16].
† Based on 5% ± 0.4 nitrogen content.
‡ Wet yarn held in tension during reaction.
** Cold stretch of the fabric after treatment.
†† Reacted yarn passed through rolls at 300° C. with 10-sec. contact.
‡‡ Reacted yarn immersed in 1% aqueous Triton X-400, dried at 100° C.

changed by cyanoethylation at substitutions up to 0.70 [13] (Table I). The strength of the individual fibers fluctuated 5–18% below that of its control, whereas the strength of the bundles showed improvements up to 5% [27]. The results are summarized in Figure 2.

The strength of cotton yarns [5, 9, 14, 16, 26] behaved quite variably upon cyanoethylation, depending on their construction (e.g., whether 2-ply yarn or 5-ply sewing thread), their amount of twist, and on the auxiliary treatments applied. The strength of 2-ply yarns (Tables II and III) was increased in all cases by substitutions up to DS 0.60. The strength of 5-ply sewing thread at substitutions up to DS 1.35 (Tables III, VI, VII) almost invariably declined, although in two cases very slight improvements were noted. In tensioned 2-ply yarns physically coated with polyacrylonitrile, improvements reached 62% in one case (Table IV), 26% in untensioned yarns, and 18–33% in yarns stretched after vapor polymerization. The results are averaged and summarized in Figure 2.

The strength of fabrics likewise varied considerably [5, 15, 20, 28], depending on the degree of substitution and type of fabric. At substitutions below 1.0, treated fabrics (8-oz. duck, 4-oz. cotton fabric, 48 × 48 sheeting, and 80 × 80 print cloth) (Tables VIII, IX, X, and XII) gained somewhat in strength. At substitutions of 1–2.67 on 80 × 80 print cloth (Tables VIII, XII, XIV) the strength (Figure 2) decreased progressively to below 70% of the control and the samples became boardy.

TABLE V. Properties of 14/2 (42 × 2 Tex) Yarns Coated with Acrylonitrile from Vapor Phase *

	Scoured control	Coated ACN	
		value	% of control
Estimated weight increase, %†	0	23.5	123.5
Flex abrasion, cycles to rupture	1060	176	17
Flat abrasion, strength retained, % after			
25 cycles	66.0	89.4	132
50 cycles	40.5	83.8	207
100 cycles	(failed)	75.8	—
rupture, log cycles	1.98	2.60	131

* Taken or recomputed from Haydel et al. [16].
† Estimated for 5% nitrogen content.

TABLE VI. Effect of Alkali Concentration and Reaction Time on Mechanical Properties of 12/5 (49.2 × 5 Tex) Sewing Thread *

Concentration of NaOH, %	Time of reaction,† min.	Substitution, degree	Weight increase, %	Breaking load		Ultimate elongation		Average relative stiffness, %	Relative toughness index, %
				Absolute, Kg.	Relative, %	Absolute, %	Relative, %		
0	0	0	0	4.26	105	11.1	90	117	94
2	30	0	0	4.04	100	12.3	100	100	100
2	30	0.15	5.1	4.31	107	13.2	107	100	114
4	30	.22	7.9	3.67	91	12.4	101	90	92
6	30	.36	12.2	3.72	92	13.3	108	85	99
8	30	.56	18.4	3.45	85	17.5	142	60	121
10	30	.92	31.7	3.40	84	28.5	232	36	195
15	30	.92	34.4	3.72	92	24.6	200	46	184
20	30	.73	27.2	3.63	90	26.5	215	42	194
30	30	.25	9.4	3.86	96	34.3	279	34	268
2	10	.28	8.2	3.99	99	12.5	102	97	101
2	20	.38	11.8	3.99	99	12.2	99	100	98
2	30	.48	15.6	3.58	89	13.7	111	80	99
2	60	.82	26.3	2.90	72	17.9	146	49	105
2	180	1.35	45.6	2.63	65	21.2	172	38	112

* Computed from data of Daul et al. [9].
† All 30-min. reactions at 25–26° C.; others at 55–60° C.

Knot Strength of Yarns

Knot breaking strength of yarns [1], determined on 5-ply sewing thread (Tables III and VII), at degrees of substitution up to 1.14, decreased about 15% (Figure 3).

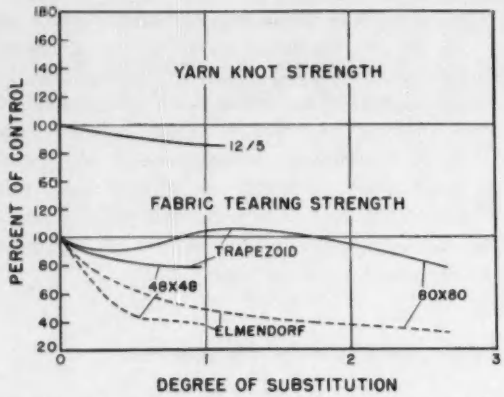

Fig. 3. Changes of cotton yarn knot strength and fabric tearing strength with degree of cyanoethylation.

Tearing Strength

Tearing strength by the trapezoid method (Figure 3) of 48 × 48 sheeting (Tables XI and XIII) decreased rapidly with cyanoethylation to 75–80% of the control at the lower substitutions; trapezoid tear values of the 80 × 80 print cloth (Table XIII) behave similarly, except that values between substitutions of 0.6 and 2.0 showed no change or perhaps a slight improvement over the appropriate control.

Tearing strength as measured by the Elmendorf method showed much greater reductions as cyanoethyl substitution increased (Tables XI and XIII).

Ultimate Elongation

The ultimate or breaking elongation of single fibers and bundles of fibers, cyanoethylated to substitutions up to 0.70, decreased to 80–90% of the controls (Figure 4).

The ultimate elongation of 2-ply yarns and 5-ply sewing threads (Figure 4), at a substitution of 0.4, usually decreased or changed relatively little (Tables

TABLE VII. Mechanical Properties of Cyanoethylated 12/5 (49.2 × 5 Tex) Sewing Thread*

Treatment	Substitution, degree	Estimated weight increase, %	Breaking load†		Ultimate elongation		Average relative stiffness, %	Relative toughness index, %	Relative knot strength,‡ %
			Absolute, g.	Relative, %	Absolute, %	Relative, %			
None	0	0	22.9	101	9.8	82	123	83	109
2% NaOH	0	0	22.6	100	12.0	100	100	100	100 (3.62)
Cyanoethylated	0.26	7.5	24.1	107	11.9	99	108	106	96
Cyanoethylated	.43	14.0	22.3	99	11.3	94	105	93	90
Cyanoethylated	.72	23.5	18.9	84	12.4	103	82	87	85
Cyanoethylated	1.14	37.2	13.6	60	18.3	152	40	91	86
Mild alkaline hydrolysis (1% NaOH, 5 min., 95° C.)									
Control	0	0	21.9	106	11.0	96	110	102	104
2% NaOH	0	0	20.6	100	11.5	100	100	100	100 (3.40)
Cyanoethylated	0.10**	3.3	21.4	104	12.2	106	98	110	105
Cyanoethylated	.20**	6.5	21.3	103	11.3	98	105	101	101
Cyanoethylated	.37**	12.1	18.3	89	12.9	112	79	100	94
Cyanoethylated	.92**	30.8	13.7	67	19.2	167	40	112	83
Severe alkaline hydrolysis (1% NaOH, 30 min., 95° C.)									
Control	0	0	22.3	106	10.9	93	114	98	106
2% NaOH	0	0	21.0	100	11.7	100	100	100	100 (3.46)
Cyanoethylated	0.01**	0.3	22.2	106	11.9	102	104	108	111
Cyanoethylated	.02**	.7	22.6	108	10.7	91	119	98	99
Cyanoethylated	.05**	1.6	18.7	89	13.0	111	80	99	92
Cyanoethylated	.07**	2.3	16.3	78	16.9	144	54	112	92

* Computed from data of Mazzeno et al. [26].
† Adjusted to basis of grams per tex of alkali-padded but unreacted controls.
‡ Values in parentheses are strengths of controls, in kilograms.
** Unhydrolyzed CN-groups; small trace COOH neglected.

II, III, VI, and VII); above this value it increased very considerably, except in samples subjected to tension in connection with the vapor phase polymer coatings. In one case (see Table VI) the elongation of 5-ply sewing thread increased nearly 180%. It is observed that elongation varied strongly, depending on whether the catalyst alkali was of mercerizing strength or not (Figure 4). It is believed that a considerable part of the increased elongation is associated with swelling and the resulting effective increase in yarn twist.

Except for a small decrease of elongation in 48 × 48 sheeting at a substitution below 0.5, cyanoethylation caused increases of 35% in the ultimate elongation of 48 × 48 sheeting and over 80% in 80 × 80 print cloth (Tables X, XII, and XIV; Figure 4).

Average Tensile and Flexural Stiffness

The average tensile stiffness of cyanoethylated single fibers and fiber bundles, at substitutions up to 0.70, remained constant or increased slightly (Table I; Figure 5), indicating in most cases a greater required load on the reacted fiber to secure the same elongation.

Changes of tensile stiffness of 2-ply yarn and 5-ply sewing thread with cyanoethylation, over a range of substitution up to and including 1.35 (Tables II, III, IV, VI, and VII; Figure 5), differed with type of product. In all cases the stiffness of 2-ply yarns, whether chemically modified or physically coated, increased within this range, whereas that of 5-ply sewing threads uniformly decreased. In the samples treated in the vapor phase (Table IV) the increases were very great and, in one case, amounted to over 400%.

With the exception of the 48 × 48 sheeting, where cyanoethylation first increased tensile stiffness at substitutions up to 0.4, it greatly decreased tensile stiffness of the fabrics (Table X; Figure 5).

Flexural stiffness [28] of a 48 × 48 sheeting (Table XI) increased progressively with substitutions, until at a DS of 0.98 it exceeded the control by approximately 150%.

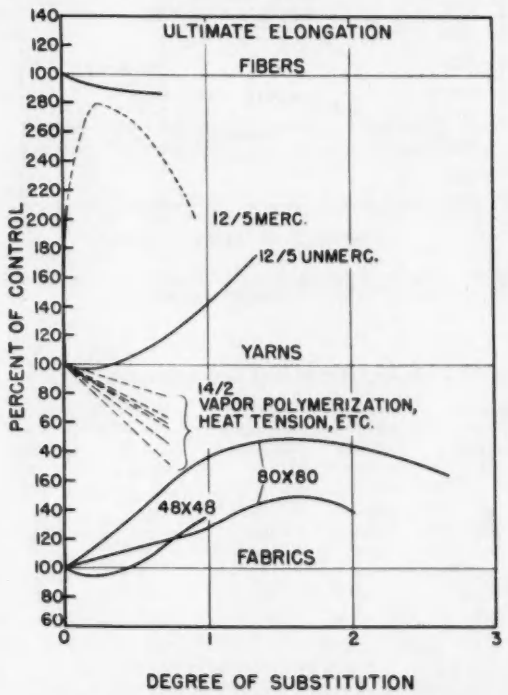

Fig. 4. Changes of ultimate elongation of cotton fibers, yarns, and fabrics with degree of cyanoethylation.

TABLE VIII. Relative Abrasion Resistance of 8-oz. Duck and 80 × 80 Print Cloth as Affected by Cyanoethylation *

Substitution, deg.	8-oz. Duck, % of control	80 × 80 Print, % of control
0	100	100
0.16	—	100
.18	108	—
.25	—	132
.32	—	109
.41	—	139
.44	164	—

* Derived from Compton et al. [5].

TABLE IX. Effect of Cyanoethylation on Strength of 4-oz. Cotton Fabric *

Substitution, degree	Breaking load,† Kg. a	b	c	av.	Relative,‡ %
0.51	24.4	24.9	24.6	24.6	100
.56	25.4	25.7	25.3	25.5	104
.59	28.4	28.6	28.0	28.3	115
.64	27.4	27.3	27.6	27.4	111
.66	28.3	28.0	28.9	28.4	115
.96	31.5	31.2	29.0	30.6	124
1.12	29.1	28.6	30.1	29.2	119

* Computed from data of Hamilton [15].
† Raveled to common number of ends.
‡ Sample of lowest addition used as basis of comparison in absence of alkali-padded control.

Toughness

The toughness index of single fibers and bundles of fibers (Table I; Figure 6) decreased irregularly to 80–90% of the control up to a substitution of 0.70. The toughness index in the 2-ply yarns was increased by cyanoethylation in most cases (Tables II and III; Figure 6) but was decreased in the case of vapor phase impregnated yarns (Table IV). The toughness of 5-ply sewing threads was increased in some cases by cyanoethylation and decreased in others (Tables III, VI, and VII), giving a negligible effect on the average (Figure 6). The improvements in toughness were very marked (168% in one case) where alkali of 10% or greater concentrations was

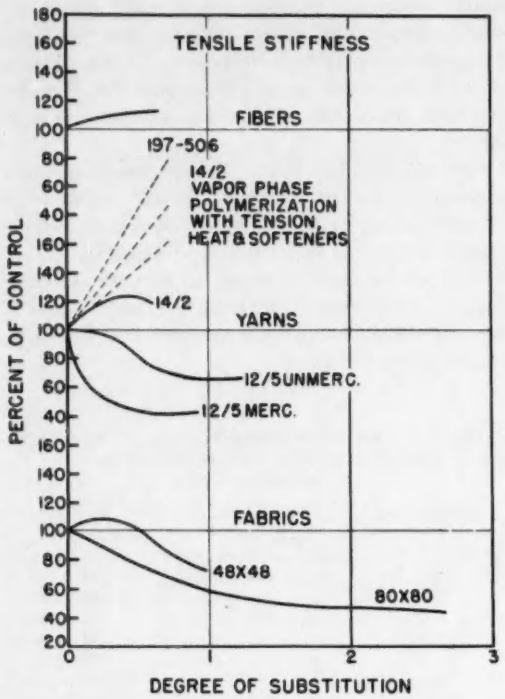

Fig. 5. Changes in tensile stiffness of cotton fibers, yarns, and fabrics with degree of cyanoethylation.

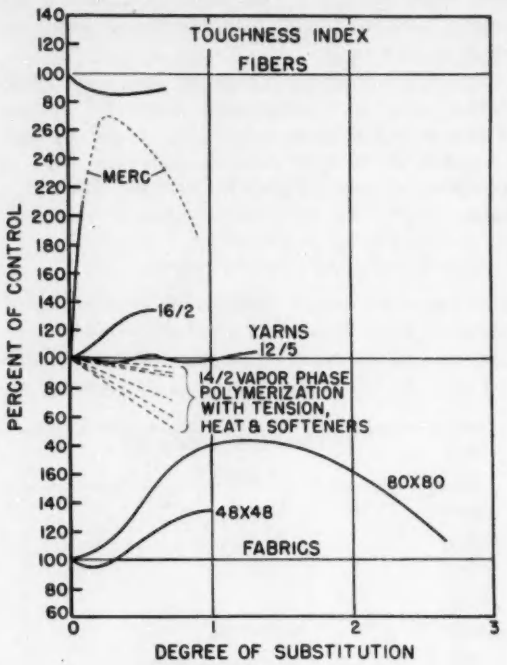

Fig. 6. Change of toughness index of cotton fibers, yarns, and fabrics with degree of cyanoethylation.

TABLE X. Mechanical Properties of Untreated and Partially Cyanoethylated 48 × 48 Cotton Sheeting *

Substitution, degree	Estimated weight increase, %	Breaking load†		Ultimate elongation		Average relative stiffness, %	Relative toughness index, %	Wrinkle recovery‡	
		Absolute, Kg.	Relative, %	Absolute, %	Relative, %			Absolute, degrees	Relative, %
0**	0	25.8	102	16.0	87	116	86	95	108
0††	0	25.3	100	18.4	100	100	100	88	100
0.27	8.82	25.3	100	17.7	96	104	96	98	111
.41	13.40	26.0	103	17.0	92	111	95	93	106
.58	18.94	25.9	102	22.0	120	86	122	76	86
.98	32.00	24.9	98	24.8	135	73	133	70	80

* Computed from data of Reinhardt et al. [28].
† Fabric raveled to 48 ends.
‡ Determined with Monsanto Wrinkle Recovery tester.[3]
** Untreated fabric.
†† Fabric received 2% NaOH pad only.

used (Table VI), due presumably to the mercerizing action and coincident change of the crystalline state of the cellulose.

The effects of cyanoethylation on the toughness of fabrics were also variable. At substitutions up to 0.4, the toughness index of the 48 × 48 sheeting (Table X; Figure 6) decreased slightly, but above this value it increased progressively up to 135% of the control at a DS of 1. One 80 × 80 print cloth, (Table XII) showed a 70–80% increase above the control between substitutions of 0.9 and 1.7. The other 80 × 80 print cloth (Table XIV), representing a less uniform product, showed only a slight increase in toughness at substitutions through 1.65, and then a reduction of toughness to 64% of the control at a substitution of about 2.0.

Elastic Recovery

The effect of cyanoethylation at substitutions of 1.04 and 1.75 on elastic recovery of 80 × 80 print cloth, studied by Janssen and others [20] (Figure 7), was to considerably improve it and permit greater strain to be applied. Thus, as the degree of substitution increased to 1.77, the elongation increased to a

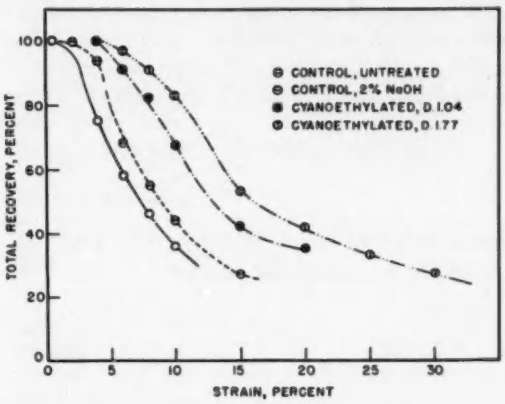

Fig. 7. Relation of total elastic recovery of untreated, alkali padded, and cyanoethylated 80 × 80 sheeting to strain.

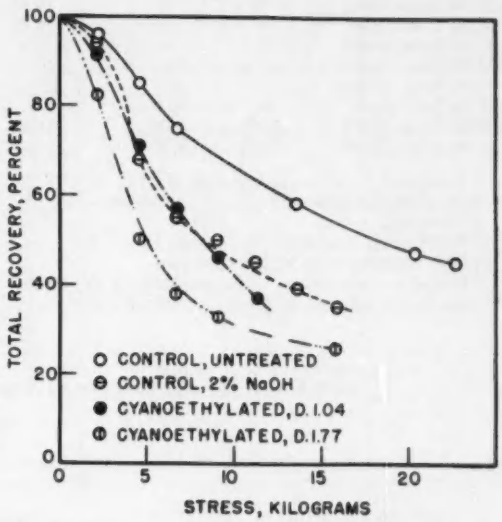

Fig. 8. Relation of total elastic recovery of untreated, alkali padded, and cyanoethylated 80 × 80 sheeting to applied stress.

TABLE XI. Certain Mechanical Properties of Partially Cyanoethylated 48 × 48 Cotton Sheeting *

Substitution, degree	Estimated weight increase, %	Tearing strength: Trapezoid Abs., Kg.	Trapezoid Rel., %	Elmendorf Abs., Kg.	Elmendorf Rel., %	Abrasion resistance: Flex† Abs., cycles	Flex† Rel., %	Flat† Abs., log cycles	Flat† Rel., %	Air permeability‡ Abs., ft.³/ft.²	Air permeability‡ Rel., %	Flexural stiffness** Abs., 10^{-4} in. lb.	Flexural stiffness** Rel., %
0††	0	3.73	89	2.18	85	964	70	1.84	94	123	176	5.2	106
0‡‡	0	4.18	100	2.55	100	1380	100	1.95	100	70	100	4.9	100
0.27	8.82	3.18	76	1.50	59	336	24	1.97	101	48	69	5.4	110
.41	13.40	3.50	84	1.14	45	219	16	1.94	99	46	66	7.2	147
.58	18.94	3.09	74	1.09	43	283	20	2.10	108	25	36	6.8	139
.98	32.00	3.09	74	1.00	39	230	17	2.13	109	12	17	12.2	249

* Computed from data of Reinhardt et al. [28].
† Determined on Stoll Universal Wear Tester.[3]
‡ Determined on Gurley Permeometer.[3]
** Determined on Tineus Olson Stiffness Tester.[3]
†† Untreated fabric.
‡‡ Fabric padded with 2% NaOH only.

TABLE XII. Mechanical Properties of Cyanoethylated Cotton Fabrics*

Fabric	Substitution, degree	Estimated weight increase, %	Breaking load†		Ultimate elongation		Average relative stiffness, %	Relative toughness index, %
			Absolute, Kg.	Relative, %	Absolute, %	Relative, %		
48 × 48 Sheeting‡	0	0	27.3	104				
48 × 48 Sheeting**	0	0	26.2	100				
48 × 48 Sheeting**	0.25	8.16	28.1	107				
48 × 48 Sheeting**	.32	10.45	29.7	113				
48 × 48 Sheeting**	.39	12.74	31.5	120				
48 × 48 Sheeting**	.44	14.36	29.8	114				
48 × 48 Sheeting**	.60	19.60	28.6	109				
80 × 80 Print cloth‡	0	0	19.8	103	15.0	88	117	91
80 × 80 Print cloth**	0	0	19.2	100	17.1	100	100	100
80 × 80 Print cloth††	0	0	20.0	100	22.4	100	100	100
80 × 80 Print cloth‡‡	0.57	18.6	20.1	105	23.9	140	75	147
80 × 80 Print cloth‡‡	.89	29.0	19.7	103	30.0	175	59	180
80 × 80 Print cloth***	1.73	56.5	18.4	92	42.1	188	49	173
80 × 80 Print cloth***	2.27	74.1	15.8	79	40.0	179	44	141
80 × 80 Print cloth***	2.67	87.2	13.6	68	36.6	164	42	112

* Computed from data of Grant et al. [14].
† Warp breaking strength.
‡ Unreacted control.
** Fabric padded with 2% NaOH only.
†† Fabric padded with 10% NaOH only.
‡‡ Reaction conducted on fabric padded with 2% NaOH.
*** Reaction conducted on fabric padded with 10% NaOH.

TABLE XIII. Tearing Strength and Abrasion Resistance of Cyanoethylated Fabrics*

Fabric	Substitution, degree	Estimated weight increase, %	Tearing strength†				Abrasion resistance			
			Trapezoid		Elmendorf		Flex		Flat	
			Absolute, Kg.	Relative, %	Absolute, Kg.	Relative, %	Absolute, cycles	Relative, %	Absolute, log cycles	Relative, %
48 × 48 Sheeting‡	0	0	3.14	85	2.82	100	876	73	2.00	105
48 × 48 Sheeting**	0	0	3.70	100	2.81	100	1200	100	1.91	100
48 × 48 Sheeting**	0.25	8.16	3.51	95	2.17	77	920	77	2.16	113
48 × 48 Sheeting**	.32	10.45	3.04	82	1.77	63	418	35	2.16	113
48 × 48 Sheeting**	.39	12.74	3.01	81	1.35	48	384	32	2.08	109
48 × 48 Sheeting**	.44	14.36	3.04	82	1.45	52	366	30	2.05	107
48 × 48 Sheeting**	.60	19.60	3.36	91	1.17	42	352	29	1.93	101
80 × 80 Print cloth‡	0	0	2.23	100	1.14	100	506	70	1.61	106
80 × 80 Print cloth**	0	0	2.23	100	1.14	100	718	100	1.52	100
80 × 80 Print cloth††	0	0	2.27	100	1.18	100	688	100	1.56	100
80 × 80 Print cloth‡‡	0.57	18.6	1.96	88	.64	56	152	21	1.61	106
80 × 80 Print cloth‡‡	.89	29.0	2.32	104	.59	52	162	23	1.76	116
80 × 80 Print cloth***	1.73	56.5	2.32	102	.46	39	258	38	2.19	140
80 × 80 Print cloth***	2.27	74.1	2.05	90	.36	31	668	98	2.35	151
80 × 80 Print cloth***	2.67	87.2	1.78	78	.32	27	557	82	2.68	172

* Computed from data of Grant et al. [14].
† Warp direction.
‡ Unreacted sample.
** Control, fabric padded with 2% NaOH only.
†† Control, fabric padded with 10% NaOH only.
‡‡ Reaction conducted on fabric padded with 2% NaOH.
*** Reaction conducted on fabric padded with 10% NaOH.

TABLE XIV. Mechanical Properties of Cyanoethylated 80 × 80 Print Cloth *

Treatment	Substitution, degree	Estimated weight increase, %	Breaking load†		Ultimate elongation		Average relative stiffness, %	Relative toughness index, %
			Absolute, Kg.	Relative, %	Absolute, %	Relative, %		
Control, untreated	0	0	25.6	100	9.7	66	151	68
Control, 2% NaOH‡	0	0	25.7	100	14.7	100	100	100
Cyanoethylated I	1.15	37.5	19.9	78	19.3	131	59	102
Cyanoethylated II	1.65	53.9	19.8	77	22.0	150	51	115
Cyanoethylated III	2.02	66.0	11.9	46	20.3	138	34	64

* Computed from data of Janssen [20].
† Warp strength adjusted to 85 threads.
‡ Padded in 2% NaOH, not reacted.

maximum of 30% with a recovery fully equal to that of the alkali treated control at only 15% strain.

In Figure 8 a somewhat different view of the elastic phenomena described above is given, since here it is shown that the untreated control and the sample treated only with 2% sodium hydroxide recover more fully at the same stress than do the samples containing cyanoethyl groups.

Wrinkle Recovery

Wrinkle recovery of 48 × 48 sheeting at substitutions up to 1 (Table X; Figure 9) was improved 5–10% above the control at low substitutions (0.25–0.40 DS) but reduced to 80% of the control at substitutions of about 1.0.

Abrasion Resistance

A very few observations made on polymer coated yarns by Haydel and others [16] by the vapor phase method (Table V) showed the flex abrasion resistance of 2-ply 14s yarns reduced to less than 20% of the control. On the other hand, this treatment improved the flat abrasion resistance in the impregnated yarn, after 25 and 50 strokes, 32 and 107%, respectively.

The flex abrasion resistance of the 48 × 48 sheetings (Tables XI and XIII; Figure 9) decreased to 20–30% of the control at a substitution of 0.60, but changed relatively little thereafter up to a substitution of 1. The flex abrasion resistance of the 80 × 80 print cloth (Table XIII; Figure 9) also decreased to about 20% of the control at a substitution of 0.6, but then improved until at a substitution of 2.67 the flex abrasion resistance was only 18% below that of the alkali padded control.

The flat abrasion resistance of 48 × 48 sheeting and 80 × 80 print cloth, expressed as log cycles

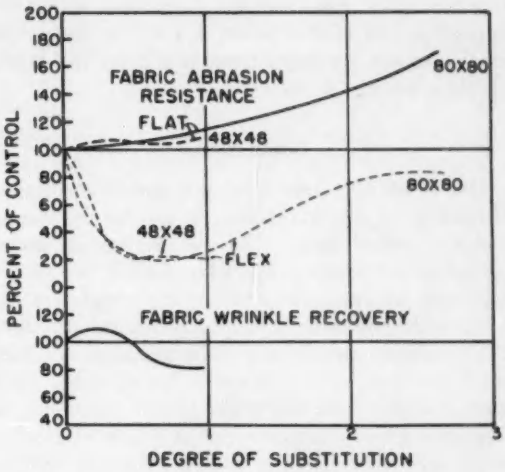

Fig. 9. Changes of cotton fabric abrasion resistance and wrinkle recovery with degree of cyanoethylation.

[30], was improved in most cases. The flat abrasion resistance of the sheetings (Tables XI and XIII; Figure 9) was increased in one case progressively with substitution to 9% above the control at a substitution of 1. In the other case it was increased to 13% above the control at a substitution of about 0.3 and then progressively less as the substitution increased to 0.6, when it was only 1% above that of the control. The number of cycles withstood in the flat abrasion test of the 80 × 80 print cloth (Table XIII; Figure 9) increased progressively with substitution to 72% above the control at a substitution of 2.67. Evidently flat abrasion resistance of cotton textiles, as commonly measured, can be greatly improved by cyanoethylation.

The dry and wet abrasion resistance of 80 × 80 print cloth (Table XV), as measured by the Ac-

TABLE XV. Effect of Cyanoethylation on Abrasion Resistance of 80 × 80 Print Cloth *

Treatment	Substitution, degree	Dry abrasion weight loss,† %	Wet abrasion weight loss,† %
Untreated control	0	0.30	1.28
Cyanoethylated, Type I	1.07–1.23	2.00	2.30
Cyanoethylated, Type III	1.85	3.03	4.78

* From data of Janssen [20].
† Determined with Accelerotor.[3]

celerotor [20], was considerably reduced by cyanoethylation. At a substitution of 1.85, the amount of dry losses was increased ten-fold and the wet losses nearly five-fold.

Discussion

One of the important limiting factors in the cyanoethylation of cotton cellulose is the heterogeneous nature of the cellulose. In the presence of dilute alkali the reaction is, presumably, limited first to the accessible regions. The latter, in the presence of the alkali which, in addition to catalyzing the reaction, also weakens the hydrogen bonds, soon becomes coated with layers of attached hydrocarbonlike ethyl groups, each capped with a CN group. Inasmuch as these side groups contain no polar hydroxyl groups, they exert relatively little mutual attraction, and as addition proceeds the cellulose structure expands in almost if not exactly direct proportion to the number of cyanoethyl groups added. This is shown by the linear decrease of density in direct proportion to addition [14] (Figure 10) and also by the fact that the density can be computed within a percent or two from the molar volumes and weights of cellulose and cyanoethyl groups and the respective densities at 25° C. of cellulose and polyacrylonitrile (cellulose, 1.55 g./cc.; oriented crystalline polyacrylonitrile, 1.14 g./cc. [18]; unoriented polyacrylonitrile, 1.04 g./cc. [10, 29]). The density of cyanoethyl cellulose is seen to lie below the density calculated from high density polyacrylonitrile but slightly above that calculated for unoriented polyacrylonitrile, suggesting a considerably more amorphous product.

As reaction continues, the accessible regions become exhausted, but the reaction does not come to a halt. Apparently kinetic movements of the cellulose segments, together with spacial interference due to attachment of the cyanoethyl groups, cause a certain strain on the anhydroglucose units of the cellulose chains in the crystalline regions; this, together with weakening of the hydrogen bonds by the alkali, permits a continual propagation of the reaction until substitutions of 2.7 or higher [9] are reached. Throughout the reaction, the CN groups present in the vicinity of the hydroxyl groups can participate in hydrogen bonding. However, the hydroxyls not only become more and more scarce as they are progressively substituted, but those remaining become isolated by the layers of hydrocarbonlike side groups. Eventually, few if any hydroxyls are in such a position as to favor hydrogen bonding, although obviously some bonding is possible between the N-atoms and neighboring hydrogen atoms. Toward the latter stages of the reaction, as small amounts of carbamoyl and carboxyl groups are produced by hydrolysis of the nitrile in the presence of water and alkali, it is probable that hydrogen bonding may occur with the nitrogen or oxygen atoms at occasional random sites.

With the information now available and the above picture of the reaction mechanism, what interpretations can be made of the observed changes in mechanical properties of fibers, yarns, and fabrics as cyanoethylation proceeds? Only limited interpretations, and these with some caution, can be made. Data for cotton fibers and fiber bundles, for which the most definite interpretations might be possible, are exceedingly limited, both in number and with respect to degrees of substitution. Attempts are

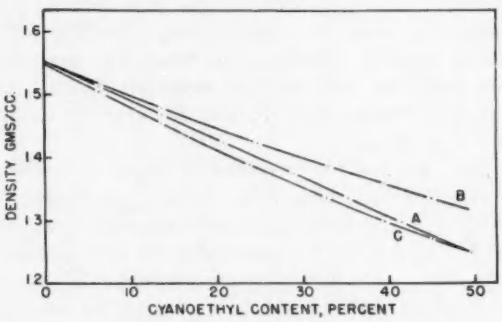

Fig. 10. Density of cyanoethylated cotton. A, observed [14]; B, computed from molar volumes and weights of cellulose and cyanoethyl, assuming the latter has the density of the fiber in polyacrylonitrile (1.14 g./cc.); C, same as B, except assuming cyanoethyl groups have density in fiber equal to that of unoriented polyacrylonitrile, i.e., 1.04 g./cc. [10].

under way to improve this situation. On the other hand, in yarns and fabrics, where much more though still inadequate data are available, associated variables complicate the conclusions. These include effects of twist, ply, change in effective twist caused by swelling of the fibers, changes in fiber fineness, changes in friction, some inevitable degradation of the cellulose, changes in yarn crimp, and in changes in fabric density, all of which react to more or less unknown degrees. Nevertheless, a few trends may be noted; these will be discussed briefly here.

One of the most evident changes that take place as cyanoethylation proceeds is that of swelling. This is shown not only by the observed linear decrease of fiber density in direct proportion to decrease of cellulose content referred to above, but also by the rapid decrease of air permeability of reacted 48 × 48 sheeting to about 37% of the control at a substitution of 0.58 and to 17% of the control at a substitution of 1.0 (Figure 11). At a substitution of 3.0, the weight increase would be 98%, giving a fiber of essentially twice the tex of its control (it is well known that the swelling of fibers is almost entirely lateral; except for a few cases as, for example, mercerization, changes in fiber length are insignificant). Since density apparently decreases linearly in direct proportion to addition, we might expect something more than a doubling of the cross section of the fiber at complete substitution or an increase of about 57.2% in diameter (square root of the product of 1.98 times the ratio of the original to final density, 1.550/1.243, expressed as percentage increase over original diameter, i.e., 1.00).

The increase of the fiber cross section due to swelling is considered to be the basis of several other observed changes in mechanical properties of textiles. It causes both an effective increase in twist factor of yarns and threads and in the stiffening of fabrics. The effective increase of ply twist multiplier was determined by Mazzeno and others [26] for a 5-ply sewing thread. That of the alkali padded control thread was 4.65, and this increased progressively to 6.2 at a substitution of 1.14 (Figure 12). These, based on the computed weight increases of 7.5, 14.0, 23.5, and 37.2%, and assuming no contraction or volume changes, correspond to the expected increases to twist multipliers of 4.83, 4.98, 5.21, and 5.50 at the corresponding substitutions, and are evidently considerably greater than those computed by Formula 3 of Landstreet et al. [22]. In addition to weight

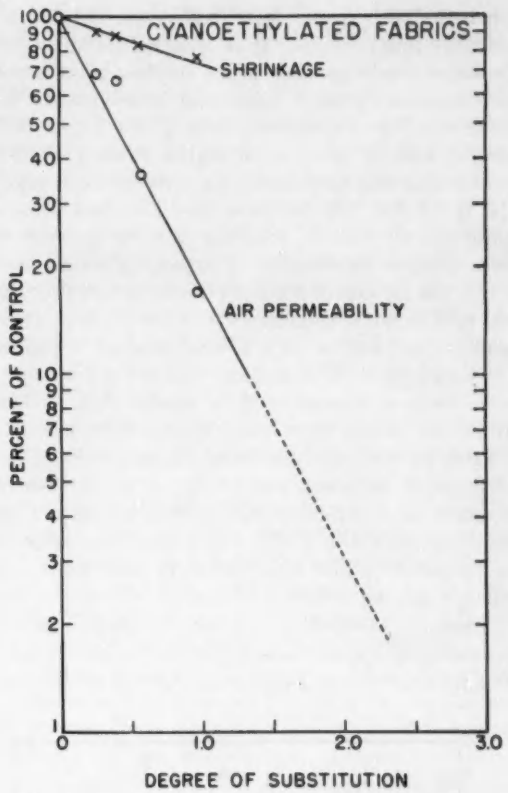

Fig. 11. Relation of air permeability and shrinkage of 48 × 48 sheeting to degree of cyanoethyl substitution [28].

increases and proportionate increases in volume, there is at the same time reduction of density (Figure 10), resulting in additional increases in volume estimated at 2.8, 4.7, 7.6, and 10.8%, respectively. This should result in somewhat greater increases of twist multipliers than computed above. Finally, there is undoubtedly some contraction in length.

It is well known that strength of the yarns is strongly dependent on twist multiplier, increasing to a maximum as twist increases to an optimum and then decreasing again as optimum twist is exceeded. As optimum twist is being approached, slippage of fiber on fiber in the yarn during stress is progressively reduced. At optimum twist, a compromise exists between some residual fiber slippage and some reduction of strength due to excessive twist and shearing action [6].

It was observed that the 2-ply low twist yarns invariably improved in strength as substitution in-

creased, whereas the 5-ply high twist threads invariably lost strength. It is believed this divergent behavior can be ascribed to the swelling effect which accompanies cyanoethylation and which pushes the relatively low twist multipliers (3.0–4.0) in both singles and ply yarns to the higher values (3.5–4.7) which approach more nearly the optimum for strength [7, 8, 12, 22]. At the same time, the fibers become progressively coarser, resulting in a displacement of the optimum twist factor to higher values of twist [11]. In the case of the 5-ply thread, at substitutions up to 1.35 swelling pushes the relatively high twist multipliers (4–5 in plys, 7–8 in singles) to values (5–6 in plys, 8–10 in singles) well beyond the optimum twist to destructive shear values. It is evident from the single fiber and bundle measurements (Table I) that relatively little change occurs in the strength of the fibers themselves. A similar loss of strength is observable in 80 × 80 print cloth at high substitutions (up to 2.67), and a similar explanation is proposed (initial twist factor in both warp and filling yarns about 4.0).

Increases in effective twist are believed to be responsible for the increases in elongation which were usually observed in 2-ply yarns (except where tension was applied during treatment), in 5-ply threads, and in all fabrics. Fiori and others [12] observed increases in elongation with increase in twist in all cases of low twist singles and doubles. This should be due both to the effect of twist itself and to contraction during spinning or twisting. In the process of reaction in fabrics, considerable contraction also occurs [28] (Figure 11); this, which is largely removable during testing, is added to the normal extensibility originally present. Similar effects have been reported by Hollihan and others [17] on cyanoethylation of viscose carboxylated rayons.

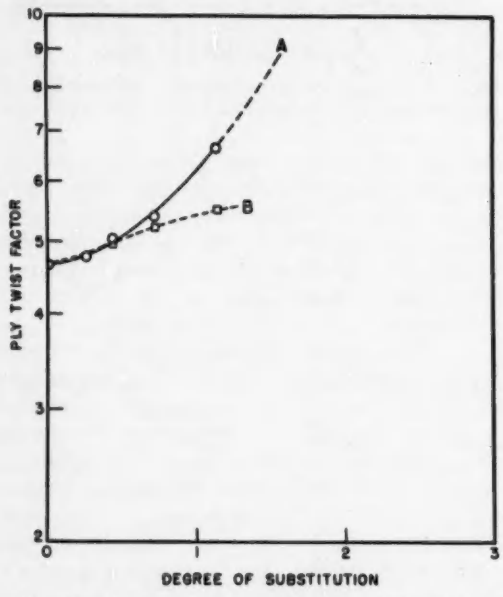

Fig. 12. Change of twist multiplier with cyanoethyl substitution. A, change observed by Mazzeno [26]; B, change computed by Formula 3 of Landstreet and others [22].

The cyanoethylation of cotton fibers and fiber bundles leads to some increase in stiffness even at low substitutions, and this is in line with expectation as coarseness of the fibers increases. On the other hand, yarns behave variably and the tensile stiffness of fabrics almost invariably decreases. This is interpreted as being associated with increases in yarn extensibility. The yarn, however, which was stretched during cyanoethylation, invariably increased greatly in stiffness, a process that is not unexpected in view of the compaction and parallelization of fiber elements which must have occurred. The increase in twist in yarns free to contract should give rise to a greater spirality with consequently lowered tensile stiffness. A decrease of stiffness in fabrics free to contract may be expected to occur on stretching, both from increased twist due to addition and from restoration of the initial length lost in shrinkage.

Still another interesting change in mechanical behavior, which may deserve comment, is the divergent behavior of abrasion resistance of fabrics. Flex abrasion resistance, relative to the control, was greatly reduced even at very low substitutions, whereas flat abrasion resistance was substantially improved. It is, of course, well recognized that the two methods differ greatly both in nature and severity. The flex test entails sharp cyclic bending of the fabric under tension, a process which a much stiffened and congested fabric evidently cannot readily withstand. The flat test, on the other hand, abrades only the surface of the fabric, which is well insulated, lubricated, or internally plasticized by the cyanoethyl groups. The over 70% increase in log cycles withstood in the flat abrasion test of the 80 × 80 print cloth may provide an important lead to possible improvements in fabrics for clothing and other textiles normally subjected to this type of action.

Summary and Conclusions

Data from different sources on the effects of different degreees of cyanoethylation on the mechanical properties of cotton textiles have been assembled, converted to comparable bases, and analyzed. In most cases results are expressed both in absolute units and in percentage change from the appropriate control.

Strength, expressed in terms of breaking load rather than tenacity in order to avoid the complicating effects of weight increases, changed variously, depending on the material (fibers, yarns, and fabrics), degree of substitution, yarn twist, and conditions during and after reaction. The strength of fibers at substitutions up to DS 0.7 was essentially unaffected. The strength of 2-ply yarns treated while relaxed increased up to 50%, while that of some physically impregnated with polyacrylonitrile, applied from the vapor phase while under tension, increased up to 62%. The strength of 5-ply sewing threads decreased at all substitutions, due to swelling and increase in twist multiplier well above the optimum. Fabric strengths increased at substitutions below 1.0 and decreased at higher substitutions.

Knot strength of 5-ply sewing thread decreased somewhat at substitutions up to 1.14, due, it is believed, to unfavorable congestion within the fine interstices of the fiber.

Tearing strength of sheeting and print cloth decreased at substitutions below 0.6 and then behaved differently depending on whether measured by trapezoid or Elmendorf methods. By the former the tearing strength of print cloth equaled that of the control between substitutions of 0.6 and 2.0, after which it decreased further to about 80% at a substitution of 2.67. Tearing strength, as measured by the Elmendorf method, decreased to 40 to 50% of the control at a substitution of 0.6 and became gradually lower as substitution increased to 2.67. In this respect the tearing behavior of the fabrics resembles that commonly observed after resin applications.

The ultimate elongation of cotton fibers decreased somewhat at substitutions up to 1.0, but that of yarns and fabrics increased in all cases, except the special case of yarns impregnated with polyacrylonitrile in conjunction with stretching treatments, conditioners, and heat.

Tensile stiffness of fibers increased somewhat, and that of 2-ply yarns impregnated in the vapor phase with polyacrylonitrile increased by over 400%. Tensile stiffness of 5-ply sewing threads decreased invariably, due to the combined swelling and twist changes.

Flexual stiffness of a 48 × 48 sheeting increased progressively to 2½ times that of the control and in a direction generally opposite to the tensile stiffness of the same fabric.

Toughness, or the ability to absorb energy when stretched, decreased somewhat for fibers, in most cases for 2-ply yarns and 5-ply sewing threads, and for fabrics, especially at intermediate substitutions (DS 1–2). However, there was a large reduction of toughness of 2-ply yarns impregnated in the vapor phase with polyacrylonitrile in various conditions of tension, heat, and softeners.

Elastic recovery per unit of strain of 80 × 80 print cloth was considerably improved by substitutions of 1 and 1.75, and maximum realizable strain was approximately doubled. However, at comparable stresses, elastic recovery was appreciably reduced and permanent set considerably increased.

Wrinkle recovery of sheeting improved about 10% at substitutions below 0.5, but decreased to 80% of the control at substitutions between 0.5 and 1.0.

Abrasion resistance of cyanoethylated yarns and fabrics changed diametrically oppositely, depending on whether the measurement was by the flex or flat method. By the flex method, abrasion resistance was reduced at very low substitutions to 20–30% of the controls, but in one print cloth sample substituted to a DS above 2 this subsequently improved until it became nearly equal to the control. On the other hand, flat abrasion resistance improved in all cases the number of cycles withstood, increasing by more than 70% in a print cloth at a substitution of 2.67.

The changes in mechanical properties are interpreted to a limited extent in terms of fiber swelling and the consequent effects of this on effective twist factor under different conditions. Internal engorgement of the fibers by the bulky cyanoethyl groups at advanced stages of substitution is offered as another phenomenon which probably explains changes in stiffness, tearing strength, and abrasion resistance.

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The Reaction of Wool With Sodium Hydroxide in Concentrated Salt Solutions

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Abstract

The properties of wool after treatment with sodium hydroxide in a series of 2 *M* aqueous salt solutions show that anions protect from alkaline degradation in the order $S_2O_3^=$, $SO_3^=$, citrate $> CO_3^= > SO_4^= > C_2H_3O_2^- > Cl^- > Br^- > NO_3^- > I^- > CNS^-$, while cations protect in the order Li^+, $Na^+ > K^+$. The swelling of wool is decreased by some 2 *M* salt solutions ($S_2O_3^=$) but is unaffected by others (CNS^-). However, the rate of sorption of OH^- by wool is the same from all the alkaline 2 *M* salt solutions and from pure NaOH. The anion concentration in solution either increases ($S_2O_3^=$) when wool is added, or is unaffected (2 *M* CNS^-); that is, water is sorbed preferentially from some salt solutions, but no specific anion sorption occurs. Salt effects on wool are therefore unlikely to be due to dehydration of the wool or to ion binding. The present results, and many other protein properties, can be simply explained on the basis of the "effective pressure" exerted by salts in solution, a concept introduced by Gibson [8].

Results of practical interest are that wool can be shrinkproofed without damage by treatment with certain aqueous sodium hydroxide solutions and that yellowing of wool in alkali can be prevented by the addition of reducing agents, such as sodium bisulfite, to the solution.

Introduction

Dilute sodium hydroxide solutions react readily with wool, the first points of attack being disulfide bonds of cystine and amide side-chains. The mechanism of the initial reaction with cystine now appears to be established [22] and, under reasonably mild conditions at least, each residue of combined cystine is converted into lanthionine [2]. Treatment of wool with weakly alkaline solutions decreases its tendency to felt [19, 24] and a moderate degree of attack markedly decreases the wet strength [18] but not the dry strength [5] of wool fibers. The feltability of wool can also be reduced by treatment in concentrated ($> 35\%$) solutions of sodium hydroxide [6], short times of treatment having no effect on the wet strength of single fibers [20] but causing an increase in dry yarn strength [3]. Much better shrinkproofing effects than these can be obtained with sodium or potassium hydroxide in organic solvents [6, 23] and, since wool is not damaged by such treatments, these processes have found industrial application.

Methods for shrinkproofing with aqueous solutions would have advantages in cost and simplicity for industrial use over those using organic solvents. It is desirable, therefore, to try to make aqueous alkaline solutions behave like those in organic solvents. A possible reason for the lack of damage in alcoholic sodium hydroxide solutions compared with similar aqueous solutions is that the swelling is much less in the former. The fact that the addition of sodium chloride decreases the swelling of wool in aqueous sodium hydroxide solutions [10] suggests that this may be a way of preventing damage, and sodium hydroxide–sodium chloride solutions do lower the feltability of wool [4]. Also, a shrinkproofing process has been claimed in which wool is treated in sodium hydroxide–sodium chloride solutions containing "accelerators" such as ammonium hydrosulfide [17].

The present paper describes studies of the reaction of wool with sodium hydroxide in concentrated aqueous salt solutions as the possible basis of a shrinkproofing method. Many tests have been car-

ried out to show whether or not treatments have an adverse effect on fabric properties. The relationship of these tests to performance in normal use is difficult to estimate, and the percentage decrease in any of the properties which can be regarded as a maximum to be tolerated is as yet a matter for individual preference. Also, a decrease in bursting strength from 114 to, say, 100 during a given treatment would be a significant change, yet fabrics manufactured to have a bursting strength of 100 may be satisfactory from the consumer's point of view. This treated fabric may then be satisfactory.

Throughout this paper, the term "damage" refers to an estimate as to whether or not tests carried out show that the properties of fabric have been significantly altered. A subjective estimate from appearance, handle, etc. of treated fabric was also made.

Experimental

Materials

Wool. The shrinkproofing treatments were carried out with samples from a scoured, plain-weave worsted fabric made from Merino 64's wool. The wool used for single fiber experiments and for sorption studies has been previously described [14, 15].

Reagents. All chemicals and solvents used were of ordinary laboratory reagent quality.

Methods

Shrinkproofing treatments. Samples of fabric, conditioned at 65% RH and 20° C., were wet out *in vacuo* in sodium hydroxide solutions at a liquor: wool ratio of 15:1. After treatment the samples were allowed to stand for 15 min. in 0.1 *N* H_2SO_4 at the same liquor ratio (alcoholic H_2SO_4 was used for samples treated in alcoholic solutions), then washed overnight in running water.

Sorption studies. During treatments as described, samples of solution were withdrawn at measured time intervals, diluted appropriately, and titrated. Sample volumes were such that titres were approximately 20 ml. of 0.1 *N* reagent. Alkali was estimated by titration with 0.1 *N* HCl to the phenolphthalein endpoint, thiocyanate was titrated with standard silver nitrate solution using ferric ammonium sulfate as indicator (after the sample had been acidified with nitric acid), chloride was estimated by Mohr's method, and thiosulfate was determined by adding an excess of standard potassium iodate solution to an acidified sample and back-titrating with standard thiosulfate solution.

Alkali solubility. Determined by the procedure of Harris and Smith [9].

Acid solubility. Determined by the procedure of Zahn and Würz [25].

Fiber Properties

30% Index. This was determined by the method of Speakman [21].

Swelling. Swelling measurements were made as described previously [16].

Fabric Properties

Reflectance measurements were made at 400 mμ using the reflectance attachment on a Unicam Spectrophotometer (Model S.P. 500) with magnesium carbonate as standard.

Felting shrinkage, yarn strength, bursting strength, and abrasion resistance were measured as described previously [14]. Bursting strengths were also measured wet, as suggested by Dr. J. H. Bradbury. Fabrics were immersed in 0.1% soap solution and then subjected to the usual bursting test. This gives an indication of the expected performance of a fabric during laundering.

Results

Preliminary Experiments

The loss in weight of wool after treatment in 0.1 *N* NaOH solutions at 65° C. was determined for times of 15 min. and longer. The initial rates of weight loss were estimated graphically and the rates relative to pure 0.1 *N* NaOH in water, taken as 100, were as follows: 2 *M* NaCl, 23; methanol, 12; saturated NaCl, 1; ethanol, 1; propanol and butanol, 0. Sodium chloride solutions therefore behave similarly to alcohols in preventing the weight loss of wool due to attack by alkali.

From preliminary shrinkproofing experiments, using 1.25 *N* NaOH solutions at 25° C., the following observations were made.

1. Shrinkproofing without damage can be obtained in solutions of the four alcohols mentioned. However, wool is damaged in methanol when treated for times only slightly longer than those necessary to give the shrinkproofing effect. Very little damage takes place in ethanol even when the time of treatment is considerably longer than that necessary for

shrinkproofing, while damage is negligible after treatment in NaOH solutions in propanol or butanol for long periods or at higher temperatures.

2. Shrinkproofing with little damage can be obtained easily in saturated NaCl, but careful control is necessary in 2 *M* NaCl; it is impossible to shrinkproof wool without damage in pure NaOH solutions in water.

Since reaction with formaldehyde protects wool from alkaline degradation [12], the effect of various formaldehyde pretreatments on the shrinkproofing of wool with aqueous NaOH solutions was investigated. These slowed down both the rate of shrinkproofing and rate of damage, but the extent of damage for a given degree of shrinkproofing was the same as that obtained on normal wool in pure NaOH solutions. Similar results were found when formaldehyde was added directly to the NaOH solutions.

Effect of Salts on the Reaction of Wool with Sodium Hydroxide

Wool samples were treated in 1.25 *N* NaOH solutions for 15 min. at 25° C. The effect of various added salts was studied using both 2 *M* and saturated solutions. Some salts were investigated more extensively, and there were no maxima or minima with regard to any of the effects measured when these were plotted against concentration.

It was found (Table I) that anions protect wool from alkaline degradation in the order $S_2O_3^=$, $SO_3^=$, citrate > $CO_3^=$ > $SO_4^=$ > $C_2H_3O_2^-$ > Cl^- > Br^- > NO_3^- > I^- > CNS^- and that the cations protect in the order Li^+, Na^+ > K^+.

The protective action of sodium and lithium salts increases with concentration. All the saturated solutions of sodium and lithium salts prevent severe alkaline degradation (Table II), saturated NaCNS being approximately equivalent to saturated $Na_2S_2O_3$ even though their relative effects at 2 *M* concentrations are very different. However, not all potassium salts show this behavior. Saturated K_2CO_3 and $KC_2H_3O_2$ solutions protect wool from alkali more than the corresponding 2 *M* solutions; saturated KCl and KBr solutions are similar to their 2 *M* solutions, while more damage occurs in saturated KCNS and KI than in their 2 *M* solutions.

The protective effect of many of the saturated salt solutions is comparable with that of the alcohols (Table II), although the rate of shrinkproofing is

TABLE I. Properties of Wool After Treatment in 1.25 *N* Sodium Hydroxide in 2 *M* Salt Solutions for 15 min. at 25° C.

Solution	Area shrinkage, %	Yarn strength	Bursting strength	Abrasion resistance, mg. wt. loss/ 1000 rev.	Acid solubility, %	Fiber swelling, %*	30% index of fibers†
(Untreated wool)	(40)	(532)	(114)	(6)	(8.0)	(18)	(0.99)
No salt	−6	222	49	90	46	77	0.10
NaCNS	−6	190	38	105	47	83	0.12
NaI	−4	272	61	94	35		
$NaNO_3$	4	324	82	60	33	61	0.29
NaBr	6	359	84	26	31		
NaCl	7	441	97	18	29	39	0.65
$NaC_2H_3O_2$	5	448	98	17	26		
Na_2SO_4 (1.9 *M*; saturated)	8	450	105	13	24		
Na_2CO_3	9	456	105	14	23		
Na citrate	10	493	107	12	21		
Na_2SO_3	9	502	107	13	21	29	0.66
$Na_2S_2O_3$	11	499	107	13	21	22	0.66
KCNS			37		56		
KI		142	44	107	50		
KBr	−7	228	79	82	48		
KCl	−2	360	82	44	44	50	0.33
$KC_2H_3O_2$	−3	365	84	20	42		
K_2CO_3	10	465	102	16	32		
LiCl	8	485	103	16	30	37	0.64
Li_2SO_4	10	491	106	13	26		

* Fibers were immersed in the required solution and the increase in diameter after 15 min. was measured.

† Fibers were stretched 30% on a Cambridge Extensometer, treated in the required solution for 15 min., washed, and restretched.

TABLE II. Properties of Wool After Treatment in 1.25 *N* Sodium Hydroxide in Saturated Salt Solutions or in Alcoholic Solutions for 15 min. at 25° C.

Solution	Area shrinkage, %	Yarn strength	Bursting strength	Abrasion resistance, mg. wt. loss/ 1000 rev.	Acid solubility, %	Fiber swelling, %	30% index of fibers
(Untreated wool)	(40)	(532)	(114)	(6)	(8.0)	(18)	(0.99)
No salt	−6	222	49	90	46	77	
9 *M* NaCNS	13	522	108	7	12	2	1.04
6.6 *M* NaI	23	513	110	8	13		
7.7 *M* $NaNO_3$	8	499	107	8	22		
7 *M* NaBr	14	552	112	8	12		
5 *M* NaCl	16	511	106	9	20	17	0.81
5 *M* $NaC_2H_3O_2$	10	540	110	12	20		
1.9 *M* Na_2SO_4	8	450	105	12	25		
2.7 *M* Na_2CO_3	4	527	106	13	30		
2 *M* Na_2SO_3	9	502	107	12	21		
4 *M* $Na_2S_2O_3$	15	569	111	8	14	9	0.94
9.7 *M* KCNS			32		67		
5.8 *M* KI			32		64		
4.5 *M* KBr	2	313	80	70	48		
4.1 *M* KCl	6	400	90	41	42	66	0.68
9 *M* $KC_2H_3O_2$	9	555	114	8	16		
5.4 *M* K_2CO_3	9	535	112	8	12		
11 *M* LiCl	21	538	113	7	10	3	0.97
3 *M* Li_2SO_4	20	529	112	9	13		
Methanol	5	530	113	7	11	7	0.95
Ethanol	6	541	113	6	10	2	0.96
Propanol	5	535	114	6	9	4	
Butanol	5	537	114	5	9	2	

less in the aqueous solutions. Much better resistance to felting without further damage can be obtained in salt solutions by increasing the time of treatment (e.g., Table V).

The swelling of fibers in the alkaline solutions is in the order that might have been expected; that is, where the wool is damaged only slightly, the swelling of fibers is small, but when the wool is extensively attacked, the fibers swell considerably. Swelling measurements on fibers in salt solutions in the absence of alkali are given in Table III. Generally, where the salt solution causes less swelling than water alone, a protective effect is observed in the alkaline solutions.

Sorption Studies

The rates at which wool sorbs alkali from salt solutions are given in Figure 1. These rates are approximately the same from pure sodium hydroxide and from sodium hydroxide in the 2 *M* salt solutions. Sorption is slower from the saturated salt solutions. No sorption could be detected from sodium hydroxide solutions in methanol or ethanol for times of 15 min. or less, but small amounts are probably sorbed, as has been shown by another method [7].

The rates of sorption of anions were also measured; in no case was any positive sorption noted. The 2 *M* thiocyanate solutions showed no change of concentration over 15 min., but both the chloride and thiosulfate solutions increased in concentration (Table IV), indicating that water was preferentially sorbed by wool. Saturated thiocyanate also showed this latter type of behavior.

Treatments of Possible Industrial Use

The properties of wool treated in saturated thiosulfate solutions of sodium hydroxide are similar to those of wool treated in alcoholic sodium hydroxide solutions (Tables II and V). The yarn strength shows a slight increase, the abrasion resistance is decreased slightly, the 30% index is lowered by 5–6%, the acid solubility is increased a little, and the felting shrinkage is decreased considerably. On the average, the bursting strengths of conditioned fabrics treated as in Table V are decreased by 1% and the bursting strengths of wet fabrics are decreased by about 6%.

The shrinkproofing reaction is much slower in thiosulfate than in alcoholic solutions, but the results in Table V show that shrinkproofed wool can be obtained under a wide variety of conditions. Some yellowing of the wool may take place in more severe treatments, but generally the color and handle of the treated wool are good.

Saturated chloride solutions would be more economical than thiosulfate, but the wool is always damaged with sodium hydroxide solutions in saturated chloride, the property most significantly altered being the bursting strength of wet fabrics, which may be decreased by as much as 20% (Tables VI and VII). However, damage is only slight after treatment under several sets of conditions, and these treatments would probably have little effect on the performance of treated wool. The results in Table VI show the range of conditions which can be used for shrinkproofing in saturated sodium chloride solutions. Lower concentrations of chloride can be used, but much more careful control is then needed to obtain satisfactory shrinkproofing with little damage. Fabrics treated as in Table VI can be bleached with peroxide with no adverse effects on the degree of shrink resistance or physical properties of the fabric. However, dyeing under various conditions decreases the shrink resistance slightly (e.g., treated fabrics which shrink 7–10% in the washing test may shrink about 12–15% after dyeing) but does not affect the physical properties. By appropriate choice of conditions, various types of fabric such as knitted jersey, worsted suitings, half-hose, and underwear fabric have been satisfactorily shrinkproofed in alkaline sodium chloride solutions.

Sodium hydroxide solutions in saturated sodium chloride invariably yellow the wool before a satisfactory degree of shrink resistance is obtained. The cause of the yellowing is not known, but it is of interest that a quantitative amino-acid analysis (carried out by Dr. J. H. Bradbury) of wool which had been treated with 2.5 *N* NaOH in saturated sodium chloride for 15 min. at 25° C. showed that only cystine had reacted, a decrease of 33% in the cystine content being found. The yellowing can be prevented, and even a slight bleach obtained, by adding small amounts of inorganic reducing agents to the solutions (Table VII). Other compounds tested and found ineffective in preventing yellowing were formaldehyde, thioglycollic acid, phenyl mercuric acetate, and hydrogen peroxide.

TABLE III. Swelling of Wool Fibers After 15 min. in Aqueous Salt Solutions and in Alcohols

Solution	Swelling,* %
Water	18
2 *M* NaCNS	19
2 *M* $NaNO_3$	16
2 *M* NaCl	14
2 *M* Na_2SO_3	14
2 *M* $Na_2S_2O_3$	12
2 *M* KCl	15
2 *M* LiCl	14
9 *M* NaCNS	10
5 *M* NaCl	7
4 *M* $Na_2S_2O_3$	6
4.1 *M* KCl	12
11 *M* LiCl	3
Methanol	12
Ethanol	2
Propanol	2
Butanol	3

* Mean of five fibers is given for each solution. The S. D. was ±1 in each case.

TABLE IV. Effect of Wool on the Concentration of Alkaline Salt Solutions. All Solutions were 1.25 *N* with Respect to NaOH. Final Concentrations were Measured After 15 min. at 25° C.

Solution	Dry weight wool, g.	Initial concentration, *M*	Final concentration, *M*	Water sorbed preferentially,* % on weight of dry wool
Water				33†
$Na_2S_2O_3$	4.982	1.997	2.039	31
$Na_2S_2O_3$ (saturated)	5.001	3.416	3.488	31
NaCl	5.012	2.016	2.049	24
NaCl (saturated)	4.993	4.782	4.868	26
NaCNS	5.007	2.011	2.010	0
NaCNS (saturated)	5.012	8.624	8.796	29

* Calculated from the increase in concentration of salt solution.

† Accepted value for water sorbed by wool from atmosphere at 100% RH or from pure water [1].

Cationic wetting agents have an adverse effect on the degree of shrink resistance obtained under a given set of conditions, but anionic and nonionic wetting agents do not affect the results.

Discussion

A possible explanation of the protective effect of certain salts on the degradation of wool by alkali would be that the decreased swelling observed in

such solutions would prevent or considerably reduce the rate of diffusion of the degradative reagent into the wool. However, the rate of sorption of OH^- ions by wool in the series of salts at 2 *M* concentrations is the same whether a protective effect is given or not (Figure 1). Also, the maximum alkali binding capacity of wool can be measured in salt solutions [15] under conditions where virtually no wool dissolves, although there has been considerable reaction with cystine. Alkali thus penetrates the wool readily and reacts with cystine, although the rate may be reduced in the saturated salt solutions. How-

TABLE V. Shrinkproofing With Sodium Hydroxide in Sodium Thiosulfate Solutions at 25° C.

Concentration $Na_2S_2O_3$, *M*	Concentration NaOH, *N*	Time, hr.	Area shrinkage, %	Yarn strength	Bursting strength		Abrasion resistance, mg. wt. loss/1000 rev.
					Conditioned*	Wet	
(Untreated wool)			(40)	(532)	(114)	(86)	(6)
4	0.25	3	21	557	115	82	8
4	0.25	6	10	556	115	82	8
2	0.75	1	3	518	109	79	9
3	0.75	1	6	524	111	80	8
4	0.75	1	7	541	114	82	8
4	1.25	0.25	15	569	115	82	8
4	1.25	2	3	531	112	80	8
4	2.5	0.25	3	542	114	82	8
4	2.5	2	1	522	109	79	9

* 20° C., 65% RH.

TABLE VI. Shrinkproofing With Sodium Hydroxide in Saturated Sodium Chloride Solutions

Concentration NaOH, *N*	Time, hr.	Temperature, ° C.	Area shrinkage, %	Bursting strength		Acid solubility, %
				Conditioned*	Wet	
(Untreated wool)			(40)	(114)	(86)	(8.0)
0.125	16	25	11	107	76	14
0.25	6	25	10	107	76	17
0.25	0.5	35	12	108	76	18
0.25	0.25	50	5	103	73	18
0.625	3	25	7	106	75	20
1.25	0.5	25	11	105	75	25
2.5	0.2	25	4	105	75	24

* 20° C., 65% RH.

TABLE VII. Effect of Inorganic Reducing Agents on the Yellowing of Wool in Sodium Hydroxide Solutions
Treatment was in 2.5 *N* NaOH in saturated NaCl for 15 min. at 25° C.

Reducing agent added	Area shrinkage, %	Reflectance, %	Bursting strength		Acid solubility, %
			Conditioned*	Wet	
(Untreated wool)	(40)	(46)	(114)	(86)	(8.0)
None	3	40	102	70	30
0.5% (wt./vol.) sodium hydrosulfite	7	46	102	72	21
2% (wt./vol.) sodium hydrosulfite	6	48	102	72	20
0.5% (wt./vol.) sodium formaldehyde sulfoxylate	5	45	104	74	22
1% (wt./vol.) sodium formaldehyde sulfoxylate	4	48	103	72	19

* 20° C., 65% RH.

ever, the wool does not swell and dissolve in some alkaline salt solutions (e.g., $S_2O_3^=$) as it does in pure sodium hydroxide or in other alkaline salt solutions (e.g., 2 *M* CNS^-).

It has generally been considered that the properties of wool in concentrated salt solutions are those of wool in an atmosphere at the relative humidity above the solutions. The wool would then contain less sorbed water and would be swollen less than in dilute aqueous solutions. However, sorption experiments show that this is not the case, either in neutral [16] or alkaline solutions (Table IV). Certain salts (e.g., $S_2O_3^=$) show a negative sorption, the amount of water sorbed preferentially from such solutions being approximately the same as that sorbed from pure water containing no dissolved salt, whereas in other cases (e.g., 2 *M* CNS^-) the solution is sorbed without change in concentration. The fully hydrated wool is swollen much less in $Na_2S_2O_3$ solutions than in water (Table III), this behavior being analogous to gelatin in sulfate solutions [16].

The effect of neutral salt solutions on the swelling of wool has been explained in terms of the "effective pressure" exerted by the salt solutions [16], a concept introduced by Gibson [8]. In solutions where ion–water interaction is high (e.g., $S_2O_3^=$) the wool is prevented from swelling (analogous to soluble compounds being "salted-out" of solution) but where ion–water interaction is low (e.g., 2 *M* CNS^-) the wool swells to about the same extent as in pure water. In this latter instance, the wool also contains the 2 *M* solution as such, and the ionic strength inside the fibers is high. These ideas can be used to explain the order of salt effects ("the lyotropic series") on many protein properties [16], to which protection from alkaline degradation can now be added. Thus, in 2 *M* thiocyanate solutions, OH^- ions penetrate wool, react, and the wool is dissolved rapidly as in pure sodium hydroxide. The ionic strength in the wool is high, facilitating configurational changes, and the effective pressure of the solution is low, allowing swelling to take place and the degraded wool to dissolve readily. In thiosulfate solutions, the situation is reversed.

When saturated salt solutions are compared, the solubility of the salts needs to be considered since, even though the effective pressure per mole may be low, that of the saturated solution may be large if the salt is highly soluble. This appears to be the case with NaCNS, when the saturated solution has a protective action equivalent to saturated $Na_2S_2O_3$. Generally, Na^+ is a more effective salting-out ion than K^+, and all the sodium salts studied give a protective effect at saturation (Table II). However, not all potassium salts show this behavior. When potassium is combined with an anion which interacts strongly with water (e.g., $CO_3^=$) the saturated solution protects wool from alkali, but where interaction of water with both ions is low (e.g., KCNS) the "effective pressure" of the saturated solution is not great enough to prevent dissolution of the wool. In these cases, the rate of degradation is rather higher than in pure sodium hydroxide ("salting-in"). This could come about by the "internal pressure" of water being lower in such solutions than in pure water, due to the large ions having separated water molecules against their own cohesive forces [13].

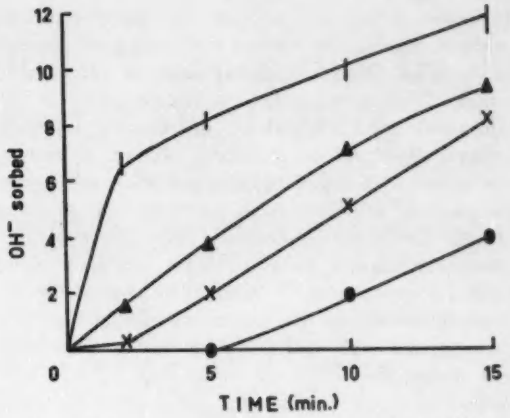

Fig. 1. Rate of sorption of OH^- ions by wool from 1.25 *N* NaOH solutions at 25° C. Units for the ordinate are g. equiv. $OH^-/10^4$ g. dry wool. I = 1.25 *N* NaOH, 1.25 *N* NaOH in 2 *M* NaCNS, 1.25 *N* NaOH in 2 *M* NaCl, 1.25 *N* NaOH in 2 *M* $Na_2S_2O_3$. (Range of values measured is shown at each time.) ● = 1.25 *N* NaOH in satd. NaCNS. ▲ = 1.25 *N* NaOH in satd. NaCl. × = 1.25 *N* NaOH in satd. $Na_2S_2O_3$. Curves for 1.25 *N* NaOH in alcohols are along abscissa.

With nonpolar or basic nonelectrolytes, Li^+ generally salts-in more than Na^+ or K^+, but with acidic nonelectrolytes (negatively charged) the effect of Li^+ is reversed [13]. This reversed behavior is really that expected on the basis of anion effects; that is, small or highly charged ions should salt-out more, due to their strong interaction with water. From this point of view, the effect of Li^+ on nonpolar solutes is anomalous. Long and McDevit [13] suggest that the very small Li^+ ions can take the place of

hydrogen atoms and fit into the water structure without causing the volume contraction which normally takes place when small ions are mixed with water. This accounts for the relative effect of Li^+, compared with Na^+ or K^+, on nonpolar nonelectrolytes or on proteins in neutral solution. However, the presence of negatively charged solutes (proteins in alkaline solution) must prevent this, allowing strong Li^+–water interaction, and therefore increased salting-out, to occur. This may come about from Li^+ ions tending to accumulate around the hydration sheath of the negatively charged groups rather than simply taking a place in the semicrystalline water structure. They may then behave "normally," as do the small anions, and contract the water structure due to the high electrostatic field strength at their surface.

Conclusion

The mechanism whereby a chemical reagent can shrinkproof wool is as yet unknown, but it seems reasonable to assume that if reaction occurs only with wool either on or near the outside of fibers, a shrinkproofing effect could be obtained without significant modification of other properties. The aim of the present work was to achieve this by lowering the degree of swelling of wool in aqueous solutions through the addition of high concentrations of inorganic salts. However, although the desired effect of shrinkproofing without damage was obtained, this was clearly *not* due to decreased swelling preventing penetration of reagent (OH^- ions) into the wool fibers.

The rate of dissolution of wool in alkaline solutions is considerably lowered by the addition of certain salts to aqueous solutions or by using alcohols as solvents. This may be due to the degradation products being less soluble in these solutions coupled with a low rate of diffusion of such products out of the fibers, which are prevented from swelling. This would mean that even though OH^- ions have readily diffused into the wool, the extent of degradation would be kept low while the shrinkproofing reaction is taking place.

Acknowledgments

I should like to thank Dr. M. Lipson, Dr. A. J. Farnworth, and Dr. J. H. Bradbury for many most helpful discussions and Miss L. Boardman for assistance with experimental work.

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A Second Order Transition Temperature in Wool Fibers in the Post-Yield Region

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Abstract

A second order transition temperature exists for stretched wool fibers in water for the temperature range 60–70° C. This transition is indicated by the transformation in certain physical properties of the fibers such as birefringence and the ability to set permanently. Below the transition temperature a fiber under constant rate of loading passes from the yield to post-yield regions at a value of extension of about 30%, which is independent of the temperature. Above the transition temperature the value of the extension increases with increase of temperature. This variation of the extension at the turnover from the yield to post-yield region with change of temperature above a transition temperature and the constancy of the extension below were shown to hold for chemically and physically modified fibers.

Introduction

In a previous paper [5] it was pointed out that wool fibers stretched in water to 40% show a transformation in certain physical properties above a temperature range of 60–70° C. Their birefringence decreases rapidly [4], while the amount of permanent set produced in a fixed time increases rapidly [3] above this temperature. Further, the remanent stress (i.e., the stress in a stretched fiber held in water for 1 hr.) at 40% extension has been shown to pass through a transition [5]. Below this temperature range the remanent stress is mainly due to stretched bonds; above this range, to entropy.

Examination of load–extension curves of single wool fibers in water [8] shows that the strain at the turnover point between the yield and post-yield regions, which is generally at approximately 30%, starts to increase rapidly above 60° C. The possibility of using this turnover point as a measurement of this second order transition in the physical properties of wool fibers is attractive because of the ease of making the measurement. To check this, load–extension experiments over a temperature range of 20–90° C. for single wool fibers in water were carried out. Further, physical and chemical treatments that are known to affect the permanent set of wool fibers were applied to single fibers and the effect on the turnover point between the yield and post-yield regions recorded.

Experimental

The load–extension curves of the wool fibers in water were determined at a constant rate of loading using a standard Cambridge Textile Extensometer. The fibers were in the form of a loop with the two ends held by a tapered plug holder, the looped end being passed over a hook. In all cases the length of the double fiber so formed was 40 mm. All the experiments were carried out in distilled water adjusted to the required temperature for each experiment. Prior to test each fiber was relaxed in water at 52–53° C. for 1 hr.

All the wool used in these experiments was from penned Corriedale sheep hand-fed for uniformity of growth of the fibers. These fibers were supplied by the Sheep Biology Laboratory of the CSIRO and have a cross-sectional area variance along their length of about 5%.

Results

The turnover point between the yield and post-yield regions of the load extension curve was defined as indicated by point A in Figure 1; i.e., the linear portions of the yield and post-yield regions

were extrapolated until they met. The extension at this turnover point was measured over a temperature range of 20–90° C. Table I is a typical set of measurements carried out on some untreated Corriedale fibers. It was found that at high rates of loading (6 g. wt./min.) the change in the extension at the turnover point with temperature was not very marked. However, when the rate of loading was reduced to 0.5 g. wt./min. a very definite change in this extension measurement was noted (see Figure 2). This change in the extension at the turnover from the yield to post-yield regions appears to start in the normal undamaged fiber around 60° C.

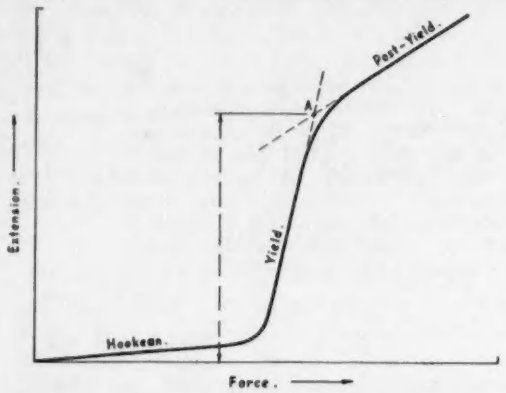

Fig. 1. A typical force–extension curve for a single wool fiber in water showing the three main regions: Hookean, yield, and post-yield. The decrimping of the fiber is omitted. The extension at the point A is taken as the value of extension at the turnover from the yield to post-yield region.

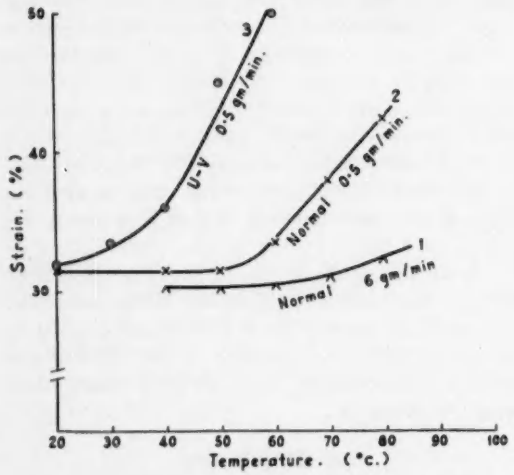

Fig. 2. A plot of the strain for a single Corriedale fiber in water at the turnover from the yield to post-yield region against the temperature. Curves 1 and 2 are for a normal unmodified fiber at two different loading rates and Curve 3 is for an ultraviolet treated fiber.

To check the relationship of the change of the turnover extension with temperature and the permanent set properties of wool, some Corriedale fibers were exposed to ultraviolet irradiation, as described previously, for a time which has been shown to substantially increase the permanent set of these fibers [6]. These fibers showed a definite change in the curve of turnover extension against temperature (see Figure 2); a transition temperature about 25° C. lower than the normal untreated fibers was obtained. Treatment in 1 *N* thioglycollic acid at pH 5 for 21 hr. at 37° C. makes the wool fibers extremely easy to set (see Table II) and also indicates from the turnover point that the transition temperature is well below room temperature. On the other hand, treatment in Van Slyke Reagent [9] or iodination [7], both of which interfere with the ability of wool fibers to set permanently, increases the temperature of the transition. In fact, at 80° C. in both cases mentioned (see Table II), the extension at the turnover point drops slightly instead of showing any tendency to increase. Further, in the case of these two treatments, the remanent stress at 100° C. (see Table II) is much higher than in the normal untreated fiber, indicating the presence of unbroken bonds.

Discussion

The extension at the turnover point between the yield and post-yield regions in the wool fibers tested shows a second order transition in the same temperature range as other physical properties of extended wool fibers, in particular the ability of the fiber to permanently set. Further, where permanent set is restricted by some chemical modification, no second order transition temperature was observed.

As mentioned previously [4], this transition for the stretched fiber is from an organized solid to an elastomeric state. Once the wool has gone into the elastomeric state, the original organized state is no longer recoverable by reduction of the temperature below the transition temperature.

This result is paralleled by evidence of the change in the x-ray diffraction pattern of stretched wet wool fibers. Astbury and Dawson [1] showed that in the case of untreated fibers the β-pattern remains after steaming the fibers stretched for 5 min., followed by

resteaming to permit contraction. On the other hand, it is well known that if fibers are stretched at room temperature in water, the α-pattern returns when the stress is removed; in fact Bendit [2] has observed that the α–β transformation is reversible when the stretching of the wool fibers is carried out at temperatures up to about 50° C., i.e., below the transition temperature. However, as previously stated, on steaming (at 100° C.), which is well above the transition temperature, the α-pattern does not reappear on contraction from the stretched β-state. Again, if the fiber is treated in Van Slyke Reagent, Astbury and Dawson [1] showed that the α-pattern does reappear after the fiber has been steamed in a stretched state.

Summarizing, we can say that when the transition temperature is exceeded in chemically unmodified wool, the α-pattern does not return on length recovery. Also, when the transition temperature is raised by chemical treatment (e.g., Van Slyke Reagent), the α-pattern does return under conditions when this would be impossible in normal wool. It is suggested that the structural modification taking place at the transition temperature is closely allied to the structural modification which results in the irreversibility of the α-pattern.

It may also be pointed out that loss of birefringence in fibers which have been stretched at temperatures in or above the transition range and then allowed to recover their length [4] is consistent with irreversibility of the α–β transformation under the same conditions. Birefringence and diffracted x-ray intensity are both measures of structural organization in the fibers.

TABLE I. The Values of the Extension at Turnover Point A for Various Wool Fibers in Water Over the Temperature Range 42–80° C.

(The load–extension curves of these fibers were carried out at a constant rate of loading of 0.5 g. wt./min.)

Temperature	42° C.	50° C.	60° C.	70° C.	80° C.
Percentage strain at the turnover point	31.0	31.5	35.0	38.5	43.0
	31.0	31.7	33.0	37.5	40.5
	31.0	32.0	33.0	38.5	41.5
	32.0	31.7	33.5	37.0	44.0
	32.0	31.0	33.7	37.0	46.5
	32.5	30.7	32.5	38.0	40.0
Average	31.6	31.4	33.5	37.8	42.6

TABLE II. The Relationship Between the Turnover Extension, the Treatment of the Wool Fibers, the Remanent Stress at 40% Extension After Boiling Stretched in Water for 1 hr., and the Permanent Set Obtained on Releasing the Fiber for a Further Hour in the Boiling Water

Treatment	Turnover point	Permanent set, %	Remanent stress at 100° C., dynes/cm.
Normal unmodified Corriedale fibers	31.5% at 20° C. 33.5% at 60° C. 42.6% at 80° C.	+ 4.0	1.43×10^7
Van Slyke Reagent	28.0% at 20° C. 26.5% at 80° C.	− 5.5	$\sim 7 \times 10^7$ at 10% extension
Iodinated (Richards and Speakman)	31.0% at 20° C. 29.5% at 80° C.	− 9.7	8.9×10^7
1 *N* Thioglycollic pH 5 37° C. for 21 hr.	>50% at 20° C.	+30.8	0.89×10^7
Ultraviolet irradiated	32.0% at 20° C. 50.0% at 60° C.	+16.4	2.4×10^7

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Chemical and Physical Effects of Finishing Cotton With Methylol Derivatives of Ethyleneurea

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Abstract

A study has been made of the mechanism by which cotton is made wrinkle resistant by dimethylol ethyleneurea. Estimates are made of the length of cross-links and the relative effect of several factors, including processing conditions, cross-linkage, and acid damage, on the loss in strength of the fabric on treatment.

Various methylol derivatives of ethyleneurea were used in the study of the effect on chemical and physical properties. It has been demonstrated that the methylol derivatives of ethyleneurea react chemically with cellulose under the influence of acidic catalysts. Metallic salts are most efficient in promoting this reaction. Both monofunctional and difunctional compounds react with the cellulose. The latter, however, cause cross-linkage, which effects marked changes in the physical properties of the treated cotton fabric, particularly wrinkle resistance. Dimethylol ethyleneurea forms cross-links averaging 1.4–1.5 ethyleneurea residues in length. These residues are connected by methylene groups. The effects of variations in catalyst, composition of the finishing agent, and curing conditions are shown. Relation of the findings to practical finishing is discussed.

Introduction

Much work has been done and is in progress at this laboratory on finishes to impart wrinkle resistance and shape-holding properties to cotton fabrics. In much of this work dimethylol ethyleneurea or, more exactly, 1,3-bis(hydroxymethyl)-2-imidazolidinone, was used as the finishing agent. The present article describes some investigations intended to give a better understanding of the reactions involved in the finishing of cotton with this agent, how variations in the finishing procedure affect these reactions, and the relation of these reactions to the properties of the finished fabric.

Experimental Procedures

Methylol derivatives of ethyleneurea were prepared in this laboratory from ethyleneurea, obtained from commercial sources, and formalin of known formaldehyde content. The ethyleneurea was dissolved in the formalin with sufficient water to give a 50% solution of the methylol compound. The solution was adjusted to pH 7–8 with sodium hydroxide solution, cooled during the exothermic reaction, and allowed to stand overnight at room temperature before dilution and application to fabric.

The fabric used in these investigations was an 80 × 80 white cotton print cloth, 3.2 oz./sq. yd., which had been desized, given an open caustic boil, and bleached. It was treated by padding with the solution of the methylol compound and catalyst, using two dips and two nips, to 70–80% wet add-on. Drying and curing were performed on pin-frames at 60° C. for 7 min. and 160° C. for 3 min. respectively unless otherwise specified. Following treatment, the fabric was given an afterwash before testing.

Test methods and analyses performed on fabric samples were:

1. Tear strength, Elmendorf, ASTM Designation D1424-56T
2. Wrinkle recovery angle, Monsanto, ASTM D1295-53T
3. Damage caused by retained chlorine, AATCC Tentative Test Method 69-1952
4. Nitrogen content, Kjeldahl method
5. Formaldehyde residues: a distillate of 160 ml. was collected from the digestion of an accurately weighed sample in 200 ml. of 25% sulfuric acid con-

[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

taining 50 g. of sodium sulfate. The formaldehyde content of the distillate was measured by the method of Yoe and Reid [8].

6. Chlorine retained after bleaching: the fabric sample was bleached in a large volume (300:1) of hypochlorite solution containing 0.02% available chlorine, rinsed, and dried in a tumble drier at medium heat. Samples of approximately 2 g. were cut into small pieces, accurately weighed, and allowed to stand 1 hr. in 200 ml. of a solution containing 10 ml. of 0.1 *N* hydrochloric acid and 2.0 g. potassium iodide, and were then titrated with standard sodium thiosulfate solution using a starch indicator. Results are expressed as the percent available chlorine where each equivalent of thiosulfate titrates 35.46 g. available chlorine.[2]

Results and Discussion

Reaction of Methylol Compounds

Like other methylol amides, the methylol derivatives of ethyleneurea, or 2-imidazolidinone, condense when heated with acidic catalysts. Since 2-imidazolidinone is difunctional, the methylol derivatives should condense to a linear water-soluble polymer. Dimethylol ethyleneurea (Figure 1), on heating in the presence of catalytic amounts of zinc nitrate, does form a solid polymer which is mostly water soluble. Analysis of the polymer shows that it contains a molar ratio of nitrogen to formaldehyde residues approximating 2.0, or one ethyleneurea residue for each formaldehyde residue. This indicates a structure of imidazolidinone rings (ethyleneurea residues) connected by methylene groups (Figure 2).

Monomethylol ethyleneurea, however, forms a product that is relatively insoluble in cold water. In fact, it can be formed by acidification of an aqueous solution of monomethylol ethyleneurea and recrystallized from water. It also has a ratio of nitrogen to formaldehyde residues of about 2.0. This suggests either a polymer of the structure suggested in Figure 2, but of considerably greater molecular weight, or a cyclic compound of relatively low molecular weight.

When a methylol ethyleneurea is heated on cotton in the presence of an acid catalyst, it is believed that polymerization is not the primary reaction but, rather, that etherification of the cellulose predominates. The reaction of methylol amides with alcohols is known [6, 7], but it is difficult to show what proportion of the material on finished cotton is actually chemically bound to the cellulose.

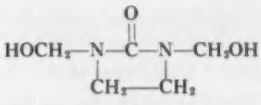

Fig. 1. Dimethylol ethyleneurea.

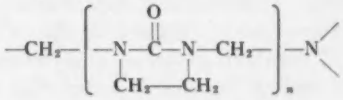

Fig. 2. Polymer of dimethylol ethyleneurea.

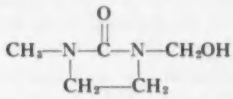

Fig. 3. 1-Methyl-3-hydroxymethyl-2-imidazolidinone.

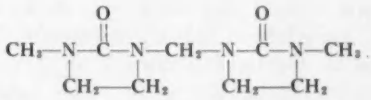

Fig. 4. Dimer of 1-methyl-3-hydroxymethyl-2-imidazolidinone.

In order to study the products from the reaction of cellulose and methylol derivatives of ethyleneurea in the presence of a minimum of condensation products, 1-methyl-3-hydroxymethyl-2-imidazolidinone (Figure 3) was used. This compound was prepared by the reaction of formaldehyde and 1-methyl-2-imidazolidinone (m.p. 114–115° C.), a new compound prepared by heating N-methylethylenediamine and ethyl carbonate. 1-Methyl-2-imidazolidinone is N-methylethyleneurea, and therefore very closely analogous to ethyleneurea. Its methylol derivative, however, contains only a single active group and cannot form a polymer. Condensation of this methylol compound by heating with an acidic catalyst gave a highly water-soluble product, melting at 129–130° C., containing 26.0% nitrogen, and yielding 13.8% formaldehyde on hydrolysis. These values show that the product is the relatively low molecular weight dimer (Figure 4), which theoretically contains 26.4% nitrogen and yields 14.2% formaldehyde. The same product was obtained by heating the methylol compound without catalysis. In no case was there formed a methylene ether, which would

[2] The authors are indebted to Dr. T. F. Cooke, American Cyanamid Company, for suggesting this procedure.

contain 23.1% nitrogen and yield 24.8% formaldehyde.

The 1-methyl-3-hydroxymethyl-2-imidazolidinone was applied to cotton under the conditions used with dimethylol ethyleneurea without catalyst and in 0.5% solutions of three catalysts: ammonium sulfate, an alkanolamine hydrochloride (Monsanto Catalyst AC),[3] and zinc nitrate. These were chosen as representative of the three classes of catalysts commonly used with methylol amides in commercial practice. The nitrogen contents of the treated fabrics after washing are shown in Table I. These data show the relative efficiencies of the catalysts, under the conditions given, in promoting etherification of the cellulose. The metallic salt was most efficient, alkanolamine hydrochloride was intermediate, and the ammonium salt least efficient. When zinc nitrate was used, about half of the applied nitrogen was retained through the afterwash. That the ether of cellulose is formed predominantly is shown not only by the appreciable nitrogen content after washing but also by the ratio of nitrogen to formaldehyde residues on the treated cotton. The dimer has a theoretical ratio, substantiated experimentally, of 4; an ether of this compound, a ratio of 2. The ratio determined on the fabric treated in the presence of zinc nitrate is 2.3. Since the ratio is higher than theoretical, by more than the experimental error is believed to be, it seems probable that some dimer has formed which is physically entrapped within the fiber and is not removable by the afterwash.

It is unlikely that any significant amount of the determined formaldehyde is due to cellulose formals produced from the formaldehyde liberated in the treatment. Zinc nitrate in the presence of such nitrogenous compounds, where the zinc probably exists as a complexed cation, does not introduce appreciable amounts of formaldehyde into cotton. However, the zinc nitrate without a complexing agent will introduce formaldehyde into cotton.

Cross-Linkage of Cellulose

Dimethylol ethyleneurea may be expected to react in a manner similar to the methylol derivative of the N-methyl analogue, described above, except that, being difunctional, it can form cross-linkages by reaction with two different cellulose molecules. It has been postulated by a number of investigators (for example, Walter, Buxbaum, and Green [6]) that the wrinkle-resistant properties of fabric treated with dimethylol ethyleneurea are dependent upon the formation of such cross-linkages. These cross-linkages would be expected to cause drastic changes in the physical properties of cotton.

Three compounds were used to investigate the effect of reaction on the wrinkle recovery and tear strength of a fabric. These were (a) dimethylol ethyleneurea (Figure 1), (b) monomethylol ethyleneurea, and (c) 1-methyl-3-hydroxymethyl-2-imidazolidinone (Figure 3). They were applied to cotton to give the properties shown in Table II. The samples with higher add-ons were applied from solutions 7% in methylol compound and 0.5% in zinc nitrate; the samples with lower add-ons were applied from a diluted solution.

Only the dimethylol compound, which can form cross-linkages, causes a large increase in wrinkle recovery. The small increase in wrinkle recovery caused by the monomethylol ethyleneurea is probably due to a small amount of dimethylol compound formed by an equilibrium in the treating bath. The 1-methyl-3-hydroxymethyl-2-imidazolidinone does not improve the wrinkle recovery at all.

Dimethylol ethyleneurea causes approximately twice the loss in tear strength that the monomethylol compound does. Since the same amount of acid catalyst is used with both agents, this larger strength loss is probably due to the cross-linkage. In an attempt to show the effect and importance of each factor causing tear strength loss in the finishing procedure, fabric was treated separately with (a) water only, (b) a 0.5% solution of zinc nitrate catalyst alone, (c) a solution of 0.5% zinc nitrate and 4% unsubstituted ethyleneurea, 2-imidazolidinone, and (d) a solution of 7% dimethylol ethyleneurea and 0.5% zinc nitrate. The sample treated with unsubstituted ethyleneurea and zinc nitrate was included to demonstrate the neutralizing action of the amido compound on the catalyst. It was not expected that this compound would react with the cellulose.

The tear strengths of these samples are compared graphically in Figure 5. A 9% loss of the original tear strength occurs when plain water is applied under the treating conditions used; application of the zinc nitrate solution causes 39% loss. If, however, ethyleneurea is present, the loss is only 24%,

[3] Throughout this paper, the mention of trade names and firms does not imply their endorsement by the Department of Agriculture over similar products or firms not mentioned.

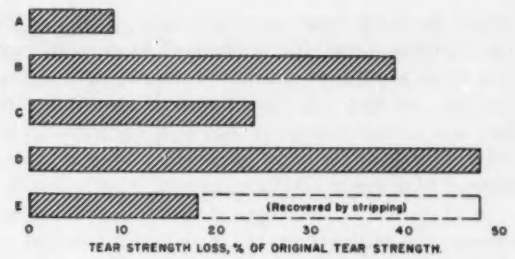

Fig. 5. Tear strength loss on treatment of 80 × 80 cotton fabric. Treatment with (A) Water only, (B) 0.5% zinc nitrate solution, (C) 4% ethyleneurea and 0.5% zinc nitrate solution, (D) 7% dimethylol ethyleneurea and 0.5% zinc nitrate solution, and (E) same treatment as (D) with finish removed with a urea-phosphoric acid solution.

because of the neutralizing effect of the nitrogenous compound. No durable material is left on the cotton by this treatment. With the complete treatment, using dimethylol ethyleneurea and zinc nitrate catalyst, a 48% loss is observed. It can be concluded, therefore, that half of this loss, 24%, is due to cross-linking while the other half is due to degradation or other effects during finishing.

A confirmation of this conclusion is observed when the resin finish is removed by a urea-phosphoric acid stripping bath, as described by Smith [4]. This stripping procedure causes an additional 2% loss in tear strength on the untreated or the water-treated fabric. The cross-linked fabric, however, recovers approximately half of the tear strength lost in the treatment, as would be expected from the conclusions drawn.

A further investigation of the cross-linking effect was made by studying the result of variation in the amount of methylol substitution on ethyleneurea. For this study, finishing agents were prepared from ethyleneurea and formaldehyde in molar ratios of CH_2O:EU ranging from 2.5:1 to 1:1. The extremes of this range correspond to monomethylol ethyleneurea and to dimethylol ethyleneurea with excess formaldehyde. These agents were applied to fabric from solutions 7% in total solids and 0.5% in zinc nitrate, with 70–80% wet add-on to give the properties shown in Table III.

The data in Table III show that, in general, the efficiency as measured by add-on, wrinkle recovery, and tear strength loss increases as the methylol substitution increases. The increase, however, is small after a substitution of 1.5 is attained. In fact, considering the lower add-on, the durable material applied with a substitution of 1.3 is almost as effective in producing wrinkle recovery as the finishes of higher substitution.

TABLE I. Nitrogen Content of Cotton Treated with 1-Methyl-3-Hydroxymethyl-2-Imidazolidinone*

Catalyst used	Nitrogen content after washing, %
None	0.17
Ammonium sulfate	0.24
Alkanolamine hydrochloride	0.44
Zinc nitrate	0.68

* Dried at 60° C. for 7 min. and cured at 160° C. for 3 min.

TABLE II. Comparison of Effect of Treatment of Cotton with Di- and Mono-Functional Derivatives of Imidazolidinones

Reactant used with cotton*	Add-on, %	Wrinkle recovery, W+F, degrees	Tear strength, W, g.
None	—	201	1012
Dimethylol ethyleneurea [Bis(hydroxymethyl)-2-imidazolidinone]	1.7	281	584
	4.5	303	520
Monomethylol ethyleneurea [Hydroxymethyl-2-imidazolidinone]	2.2	211	746
	2.7	217	704
1-Methyl-3-hydroxymethyl-2-imidazolidinone	2.3	198	—
	3.6	205	—

* Zinc nitrate catalyst-dried 7 min. at 60° C. and cured for 3 min. at 160° C.

TABLE III. Effect of Methylol Substitution on Properties of Finished Cotton Fabric

Methylol groups per ethyleneurea	Add-on,* %	Wrinkle recovery, W + F, degrees	Tear strength, W, g.
Untreated fabric	—	201	1012
1.0	2.2	211	746
1.3	2.8	281	540
1.5	4.7	292	528
1.8	4.0	296	536
2.0	4.5	303	520
2.5	3.9	305	496

* Dried 7 min. at 60° C., cured 3 min. at 160° C.

Composition of the Finish

An investigation was conducted to determine the chemical constitution of the finish, that is, the actual material on the cotton fabric, obtained by treatment with dimethylol ethyleneurea. Steele and Giddings [5], by determination of the ratio of formaldehyde residues to urea, on fabric treated with methylol urea, were able to assign a chemical structure to the finish. A similar ratio was determined in the present case. The ethyleneurea residues on the finished fabric were estimated from the nitrogen content, and the formaldehyde residues from the formaldehyde released on acid hydrolysis of a sample of the fabric. From these values, the ratio of formaldehyde residues to ethyleneurea residues was calculated.

The formaldehyde residues exist in the finish either as methylene groups between two ethyleneurea residues (see Figure 2) or as methylene ether groups between an ethyleneurea residue and cellulose. It is believed that no free methylol groups are present, as they are not stable enough as such to be retained through the finishing procedure. This conclusion is based on the properties of the methylol compounds observed while working with them and is borne out by subsequent data (Table VI).

Unfortunately, no method was found that could be used for distinguishing between methylene and methylene ether groups. This prevented a more definite determination of the structure of the finish.

In the interpretation of the determined ratio, the following points were considered. An ethyleneurea-formaldehyde polymer, of the structure shown in Figure 2, will have a ratio of formaldehyde residues to ethyleneurea residues of between 0.5 and 1.0, depending upon the degree of polymerization. It is expected that most, but not all, of any polymer formed in the fiber will be removed by the afterwash. In the interpretation of the ratios, it is assumed that values due to polymer are negligible. That part of the finishing agent that is involved in cross-linkage will have a ratio of formaldehyde to ethyleneurea residues between 1.0 and 2.0. A general structure for such a cross-linkage is shown in Figure 6. The value of 2.0 for the ratio is obtained when a cross-linkage of a single ethyleneurea unit exists—that is, n equals zero. As the length of the cross-linkages increases, the ratio decreases. Any material bound to the cellulose but not forming a cross-linkage will show a ratio of 1.0 whether bound as a single unit or as a graft polymer.

Samples of fabric treated with dimethylol ethyleneurea and zinc nitrate, using the treating procedure described, have a ratio of formaldehyde residues to ethyleneurea residues of 1.7. This value will vary somewhat at different add-ons. Assuming that, in this case, all the bound material is involved in cross-linkage, the average length of the cross-linkages is 1.4–1.5 ethyleneurea residues. In Figure 6, then, n has an average value between 0.4 and 0.5. This means that the majority of the cross-linkages are probably either one or two ethyleneurea residues in length.

Although it is true that the theoretical maximum number of cross-linkages is limited by the number of dimethylol ethyleneurea molecules present, the practical result of having monomethylol ethyleneurea present in a treating bath is to increase the number of cross-linkages that can be formed from the same amount of the dimethylol compound. The monomethylol ethyleneurea can enter into the formation of multiple unit cross-linkages in place of the dimethylol compound. The dimethylol ethyleneurea so replaced can then form additional cross-linkages. This explains the high wrinkle recovery obtained with relatively low methylol substitution on the samples shown in Table III.

Even though monomethylol ethyleneurea can enter into cross-linkages, it should be expected that as the degree of methylol substitution on the ethyleneurea is reduced in a mixture, the amount of material in the finish that is chemically bound but does not form cross-linkages will increase. This should appear as a reduced ratio of formaldehyde to ethyleneurea residues in the finish. Furthermore, as this singly bound material provides sites for chloramine formation on partially substituted amido groups, an increased amount of chlorine should be retained from treatment with a hypochlorite bleach. The data in

TABLE IV. Retention of Chlorine by Fabrics Treated with Ethyleneurea of Different Methylol Content

Methylol groups per ethyleneurea	Add-on, %	Molar ratio CH_2O/EU residues on fabric	Breaking strength after scorch, % of original	Available chlorine on bleached fabric, %
Untreated fabric	—	—	95	0.04
2.0	4.5	1.7	94	0.09
1.5	4.7	1.3	90	0.15
1.0	2.2	1.0	13	0.24

Table IV obtained on samples treated as before with zinc nitrate catalysts show that both of these conclusions are correct. As the methylol substitution is decreased the ratio decreases, and both the amount of retained chlorine and damage in the scorch test are increased.

The amount of chlorine retained by the finish gives an approximate determination of the unsubstituted groups. The small amount of chlorine retained by the dimethylol ethyleneurea, with a substitution of 2, supports the assumption that with this agent there is little bound material not involved in the cross-linkages.

Since it was noted with 1-methyl-3-hydroxymethyl-2-imidazolidinone that different catalysts give different degrees of etherification of cellulose (Table I), it would be expected that noticeable differences would be observed between dimethylol ethyleneurea finishes applied with different catalysts. By use of the same three catalysts, with 0.5% catalyst solids in solution, the fabric properties shown in Table V were obtained. The differences in wrinkle recovery and tear strength values are not great with the treating conditions used, but the ratio of formaldehyde to ethyleneurea residues changes considerably with the catalyst. With the ammonium salt, therefore, a greater percentage of the add-on consists of bound but not cross-linking material.

In Table VI are shown the chlorine retentions of finishes prepared with the three catalysts and an ethyleneurea substituted to an average of 1.8 methylol groups. This lower substitution was selected to emphasize the differences among the catalysts. The chlorine retention data support the conclusion that proportionally fewer cross-linkages are formed with the ammonium salt and the alkanolamine hydrochloride than with the metallic salt. It is because of the higher efficiency in promoting etherification, hence cross-linking, that metallic salt catalysts minimize chlorine damage with nitrogenous finishes, rather than by neutralization of acid by metallic residues as has been previously postulated [1].

TABLE V. Effect of Different Catalysts on the Treatment of Cotton with Dimethylol Ethyleneurea

Catalyst	Add-on, %	Wrinkle recovery, W + F, degrees	Tear strength, W, g.	Molar ratio CH_2O/EU in finish
Ammonium sulfate	6.3	306	544	1.4
Alkanolamine hydrochloride	6.8	313	524	1.5
Zinc nitrate	6.6	311	484	1.7

TABLE VI. Retention of Chlorine by Fabrics Treated with a Methylol Ethyleneurea* Using Different Catalysts

Catalyst	Add-on, %	Breaking strength after scorching, % of original	Available chlorine on bleached fabric, %
Ammonium sulfate	3.7	24	0.22
Alkanolamine hydrochloride	3.0	108	0.19
Zinc nitrate	3.8	105	0.11

* Methylol substitution 1.8.

Another factor that would be expected to affect the composition and properties of the finish is variation in curing conditions. In Table VII are presented the properties of fabrics treated with a solution 7% in dimethylol ethyleneurea and 0.5% in zinc nitrate that have been cured for different times and at different temperatures after the usual drying. It is shown that at 160° C., the curing temperature used in most of this investigation, a rapid cure is obtained, the cure being complete within a minute. At intermediate stages of cure, incomplete reaction is obtained, evidenced mainly by the increased chlorine retention. This is probably due again to the presence of bound but not cross-linking material. At lower temperatures of cure, the reaction proceeds more slowly, as expected, with greater chlorine retention shown at equal times of cure. These results show

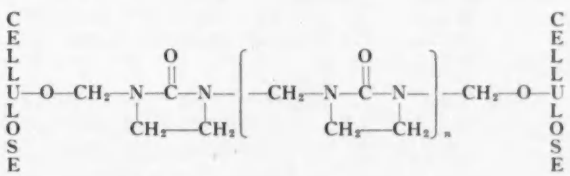

Fig. 6. Ethyleneurea cross-linkage of cellulose.

that it is unwise to use crease recovery only as a criterion for completeness of curing. Curing that is sufficient to produce good wrinkle recovery can, nevertheless, leave enough partially reacted groups to cause an appreciable increase in chlorine retention.

In the case of the samples shown in Table VII, it was not possible to follow the course of the reaction by determining the ratio of formaldehyde residues to ethyleneurea residues. Almost the same ratio was obtained with all samples. This failure of the method may be due to the mild cure failing to remove unreacted methylol groups, thereby causing the formaldehyde values to be high on the basis used for interpretation of the ratio.

Effect of Laundering on Finish

Other workers in this laboratory [2, 3] have found that the ethyleneurea finish has good stability toward home-type laundering as well as toward commercial laundering if a pH lower than 4 is avoided in the souring step. In the present investigation, the effect of laundering on the composition and properties of the finish, particularly chlorine retention, was studied more closely. For this purpose, one set of samples of cotton treated with dimethylol ethyleneurea, using zinc nitrate catalyst as before, was submitted to 12 home-type launderings, in an automatic washing machine, with bleach added in each laundering and a similar set was submitted to the more drastic high temperature laundering, described in AATCC Test 14-53.

The changes in properties of the finished fabric caused by the launderings are shown in Table VIII. Neither type of laundering causes a significant change in the amount of finish present or in the breaking strength of the fabric. Also, the ratio of formaldehyde to ethyleneurea residues remains constant at 1.7. Chlorine retention, however, has been materially increased by the AATCC laundry procedure. The increase of chlorine retention is slight, but evident, with the home-type laundering, and might become serious after many cycles.

At first thought, it would seem probable that the increase in chlorine retention is due to partial hydrolysis of cross-linkages by the vigorous laundering, leaving ethyleneurea residues bound at one end only. The methylol groups formed by such a hydrolysis, however, would probably be cleaved and released as formaldehyde. The ratio of formalde-

TABLE VII. Change of Properties with Curing Conditions of Cotton Fabric Treated with Dimethylol Ethyleneurea

Cure*					
Temperature, °C.	Time, min.	Nitrogen content, %	Wrinkle recovery, W + F, deg.	Available chlorine content after bleach, %	Breaking strength after scorch, % of original
—	—	0.49	221	0.16	25
110	0.5	0.62	236	0.23	22
135	0.5	0.96	284	0.16	70
160	0.5	0.84	289	0.10	99
160	1.0	0.86	283	0.11	103
160	3.0	0.85	286	0.11	104

* All samples dried at 60° C. for 7 min. prior to cure.

TABLE VIII. Effect of Laundering on a Cotton Fabric Treated with Dimethylol Ethyleneurea

	Wrinkle recovery, W + F, degrees	Nitrogen content, % of original	Breaking strength, % of original	Molar ratio CH_2O/EU residues	Available chlorine after bleach, %	Breaking strength after scorch, % of original
Original treated fabric (control)	303	100	100	1.7	0.09	94
After 12 home-type launderings	288	97	92	1.7	0.12	101
After 5 AATCC 14–53 launderings	288	97	103	1.7	0.23	74

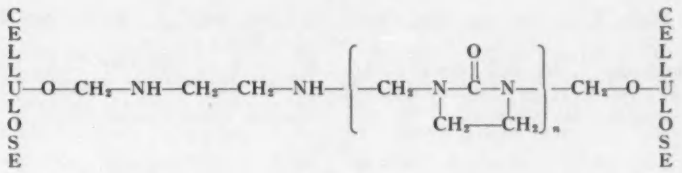

Fig. 7. Possible hydrolysis product of ethyleneurea cross-linked cellulose.

hyde to ethyleneurea residues, then, would decrease; such a decrease is not observed. Furthermore, it seems probable that there would be complete hydrolysis of some groups, as well as the partial hydrolysis, and a significant loss of nitrogen would be observed. It is believed, therefore, that the increased chlorine retention after laundering is due not to hydrolytic cleavage of cross-linkages but to cleavage of ethyleneurea rings. The number of cross-linkages is unchanged, but some of them are chemically modified, possibly by conversion of ethyleneurea units to ethylenediamine units, as illustrated in Figure 7. Such units would have sites where chloramine formation could occur. Supporting this hypothesis is the relatively small loss in strength on scorching for the amount of chlorine retained after bleaching. The presence of amino groups would partially neutralize the hydrochloric acid released and reduce the amount of resultant degradation.

Summary

A study has been made of the reactions that occur when methylol derivatives of ethyleneurea, or 2-imidazolidinone, are applied to cotton fabric and the relation of these reactions to the properties of the finished fabrics.

By the use of the methylol derivative of N-methylethyleneurea, 1-methyl-3-hydroxymethyl-2-imidazolidinone, it is shown that methylol compounds of this type undergo an etherification reaction with cellulose. This reaction is promoted by acidic catalysts, of which zinc nitrate is more effective than an alkanolamine hydrochloride and ammonium sulfate is less effective. The methylol compounds also condense with themselves, forming condensates in which the ethyleneurea residues are connected by methylene bridges.

When dimethylol ethyleneurea is applied to cotton, etherification of the cellulose occurs. Since this reagent is difunctional, the cellulose is cross-linked by the reaction. The cross-linkages formed average 1.4–1.5 ethyleneurea residues in length, with methylene bridges between ethyleneurea residues. It is the cross-linking of the cellulose that is responsible for the wrinkle resistance imparted by the finish. The cross-linking of the cellulose also causes a loss in tear strength that is in addition to that caused by acid and heat degradation in the finishing process. On the fabric used in this study, it was found that about half of the total loss in tear strength was due directly to the cross-linking.

A dimethylol ethyleneurea finish shows little chlorine retention if properly applied. Chlorine retention, however, will be increased if the dimethylol compound reacts less completely. This can be caused by inefficient catalysis, incomplete curing, or the use of an agent containing a lower methylol substitution than the dimethylol compound. The increased chlorine retention is caused by an increased amount of ethyleneurea that is bound to the cotton but does not form cross-linkages. Each of such ethyleneurea residues has an amido nitrogen that is only partially substituted and can, therefore, form a chloramine.

Vigorous and repeated laundering can also increase the chlorine retention of a dimethylol ethyleneurea finish. In this case, hydrolysis occurs which does not cleave cross-linkages but modifies them so that chloramine formation can occur.

Acknowledgment

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The Relation Between Crystallite Orientation and Tensile Properties of Mercerized Cotton

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Introduction

It is well known that cotton, like other textile fibers, becomes stronger, stiffer, and less extensible with increasing molecular orientation [2, 10, 11]. However, orientation by itself does not fully account for the difference in strength and extensibility of different cottons. Tensile properties can be affected by a number of other factors such as the pattern of weak links in the fiber, which may differ from cotton to cotton. The present study was undertaken with the object of minimizing the effect of factors which may contribute to intercotton differences and highlighting the effect on tensile properties of structural parameters like crystallinity and orientation. For this purpose, the fine structure of each of several varieties of raw cotton was changed in a controlled manner by means of mercerization under varying degrees of stretch. The word "mercerization" as used in this paper does not denote the commercial process. It is used as a convenient single word for describing the sequence of swelling slack fibers with caustic soda, stretching them to a predetermined length, washing the fibers free of caustic soda while under stretch, and finally conditioning them to the laboratory atmosphere. The crystallite orientation, tensile strength, and extensibility of fibers prepared in this manner and the relationships between these properties are described in the present paper. Apart from fundamental aspects, it is hoped that the data now presented may also have some applied value in view of the large amount of current work on modifying cottons with the help of intracrystalline swelling agents [13].

Selection and Preparation of Cottons

The cottons used in this study were selected on the basis of two considerations: their representative range of initial orientations and their good fiber length, which made it convenient to handle them. The selections covered Sea Island, Egyptian, and American varieties, with a range of crystallite orientation factor from 0.82 to 0.69. It was difficult to work with the available cottons which had even lower orientation factors, because in these cases the fibers were inconveniently short.

The ideal plan of experiment would have been to mercerize single fibers under controlled stretch and to measure their orientation, breaking stress, and strain. On account of the obvious practical difficulties of this approach, bundles of parallel fibers were mercerized instead. For this purpose, wide, flat bundles had to be prepared weighing over 50 mg./in. and with a high degree of fiber parallelization. A bundle was first prepared with the left ends of the fibers lined up. This was done by hand in the case of the longer cottons and with the help of a comb sorter in the case of the shorter cottons. The aligned left end was gripped in a stainless steel jaw, and the fibers which were not caught in the nip were gently combed out. The right end of the bundle was trimmed off so that most of the fibers would reach the trimmed end. The bundle was now drawn

through a fine-toothed comb till only a few millimeters of fiber at the free end protruded beyond the comb. The free right end was clamped in another stainless steel jaw. The left jaw was then opened and fibers which did not reach up to the nip of the right jaw were combed out. The process of parallelizing was repeated. These manipulations were performed with the jaws mounted between carefully machined rails on a platform to which the comb was fixed. The rails prevented the jaws from moving sideways while the fibers were drawn through the comb. Figure 1 is a self-explanatory photograph of the device.

The above process, with repetitions when necessary, gave accurately parallel bundles containing enough fibers for subsequent experiments. Parallelism could be critically judged by verifying that most of the fibers straightened simultaneously on the gradual application of load. The stainless steel jaws were machined so that fiber nips were localized within a fraction of a millimeter, and there was little ambiguity about the test length.

Mercerization

The Instron tensile tester was used in mercerizing the fiber bundles on account of its capacity for the accurate control of length and for the measurement of loads developed during stretching. Special adaptors were made by means of which the fiber-carrying jaws could be attached to the load cell C (1–50 Kg. range) and the cross-head of the Instron. The jaws were surrounded by a plastic enclosure inside which the stretched fibers could be washed. Figure 2 is a photograph of the arrangement used.

The mercerizing sequence was as follows. The bundle length prior to mercerizing was measured on the gauge length dial of the Instron with the bundle under a decrimping tension of 100 g. The jaws were then removed and the bundle soaked in caustic soda of 25% strength. This strength was known to be in the optimum range for securing complete swelling at the laboratory temperature of 27° C. [14]. During swelling, the fibers were allowed to contract freely. After 10 min., the bundle was transferred to the Instron and stretched by the manual control until a tension of 100 g. was recorded. The bundle length at this tension, which will henceforth be called the slack length, was read on the gauge length dial. This length gave a consistent measure of the contraction during swelling. Thereafter, the bundle was stretched to the required extent at a constant rate of 2 cm./min. The stretch length was preset as a required fraction of the initial dry bundle length. When the fibers were fully stretched, they were washed for 10 min. in a gentle stream of water. Afterwards, they were dismounted, soured in very mild acetic acid, washed again, and conditioned to the testing atmosphere. During removal of the fibers from the jaws, broken fibers, if any, were carefully teased out.

In successive experiments, the stretch on the alkali-swollen bundle was increased by 2.5 or 5% (with respect to the original length) until the stretch became high enough (10–15%) to break a perceptible number of fibers in the bundle. Figure

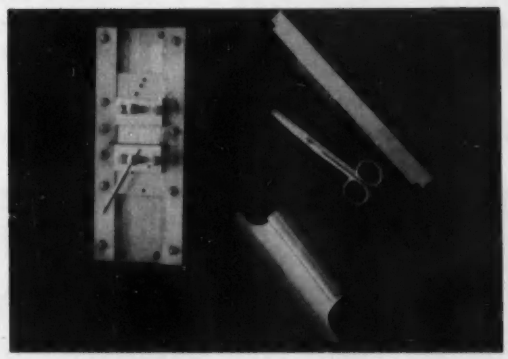

Fig. 1. Apparatus for preparing parallel fiber bundles for mercerization.

Fig. 2. Arrangement for stretching and washing alkali-swollen fibers on the Instron tensile tester.

3 gives typical x-ray diffraction photographs of the treated fibers at a few stretches. These photographs show that the cellulose in all cases is mostly converted to cellulose II and that orientation is highly sensitive to stretch. Quantitative measurements on the photographs would also have shown a decrease in crystallinity as compared to the unmercerized fiber.

The Measurement of Orientation

The crystallite orientation of the mercerized fibers was measured by x-ray diffraction. In theory, the method of measurement used would pertain only to the crystalline components of the fiber. The accepted parameter for characterizing the orientation of the crystallites with respect to the fiber axis is the x-ray orientation factor of Hermans [4], defined as

$$F(x) = 1 - \tfrac{3}{2}\,\overline{\sin^2 \alpha} \qquad (1)$$

where α is the angle made by the chain axis of each crystallite with the fiber axis and the bar sign indicates a weighted mean over all crystallites found in the fiber. Hermans and coworkers have shown that for cellulose II crystallites,

$$\overline{\sin^2 \alpha} \doteq \frac{\int_0^{2\pi} I(\beta) \cos \beta \sin^2 \beta d\beta}{\int_0^{2\pi} I(\beta) \cos \beta d\beta} + \frac{\int_0^{2\pi} I(\gamma) \cos \gamma \sin^2 \gamma d\gamma}{\int_0^{2\pi} I(\gamma) \cos \gamma d\gamma} \qquad (2)$$

In this expression, $I(\beta)$ and $I(\gamma)$ are the intensities of the $(10\bar{1})$ and (101) equatorial interferences at angles β and γ from the equator of a conventional fiber diffraction pattern on flat films.

The intensity distributions $I(\beta)$ and $I(\gamma)$ were measured by means of a Geiger counter diffractom-

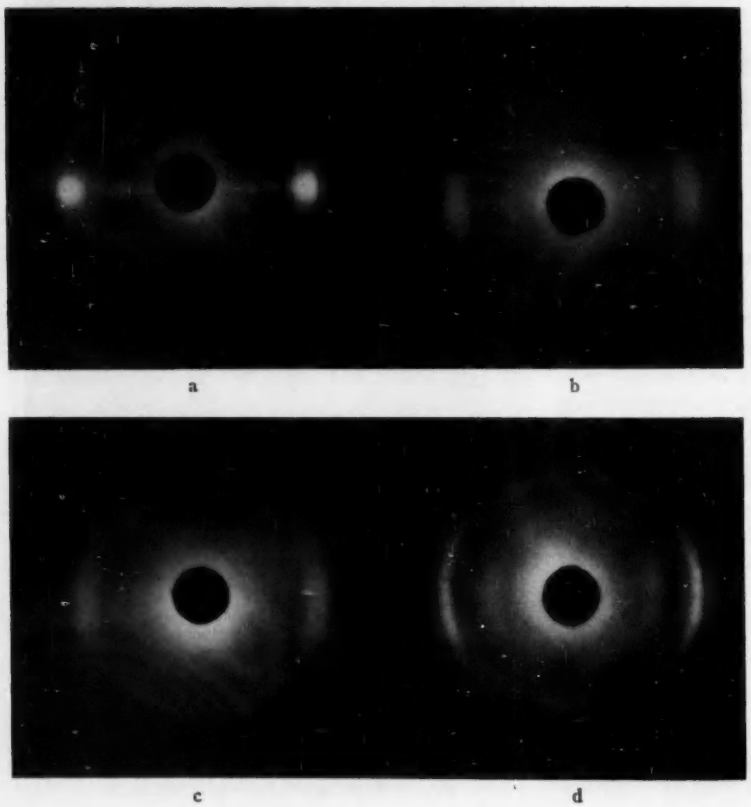

Fig. 3. X-ray diffraction patterns of Menoufi fibers unmercerized and mercerized at three different stretches. (a) Stretched to 10% over original length, (b) stretched to original length, (c) unstretched, (d) unmercerized.

eter, which was made for this purpose. The instrument is similar in principle to previously published designs [3, 8, 12] and will not be described in detail. It consisted essentially of (1) a stabilized generator giving nickel-filtered copper radiation, (2) a device for slowly rotating a bundle of parallel fibers around the incident collimated x-ray beam as an axis, and (3) a Geiger counter with a pin-hole window, which was kept fixed at the required scattering angle. During the specimen rotation, various portions of the chosen diffraction arc would sweep past the counter window. The diffracted intensities were registered by a counting rate meter which was connected to a recorder. Thus an automatic scan of the intensity distributions $I(\beta)$ and $I(\gamma)$, superposed on the background counting rate, could be obtained.

The rotating specimen mount contained a face plate on which grooves were cut in order to accommodate the fiber jaws. The bottom face of each jaw was machined to provide a rectangular groove 1 mm. wide and deep while the top face was machined to provide a tongue which would exactly fit into this groove. A weighed amount of roughly parallel fibers from the mercerized lot was mounted into one of these jaws. The protruding bundle was combed out and drawn with forceps into the groove of the other jaw. The top face was then inserted and screwed down. With a little practice, very parallel fiber bundles could be obtained. The jaws were drawn apart till the bundle was just taut and restrained in this position by springs. These techniques ensured that in successive experiments bundles with roughly the same density (about 5 mg./in.) could be packed to roughly the same geometry (1 mm. width and reasonably constant thickness) and truly centered over the x-ray beam. A photograph of the instrument is shown in Figure 4. The angular divergence of the collimated x-ray beam, the aperture of the Geiger counter window, the speed of specimen rotation, and the time constant of the rate meter were all carefully selected so that there would be reasonable fidelity in the records of intensity distribution.

The computations were made as follows. The recorded scans were smoothed out and corrected for nonlinearity of the counter. The background intensity was visually estimated and subtracted from the diffracted intensity at each azimuth angle. The differences were expressed as fractions of the counting rate at zero azimuth angle. These values were then plotted against the corresponding angles and a smooth line drawn through the points. Typical results are shown in Figure 5. From these reduced curves of $I(\beta)$ and $I(\gamma)$ the integrals in Equation 2 were evaluated numerically. Analytical expressions were also sought for the curves which would make the functions in Equation 2 readily integrable, but this attempt was not quite successful.

It may not be out of place here to discuss briefly some of the errors involved in calculating the orienta-

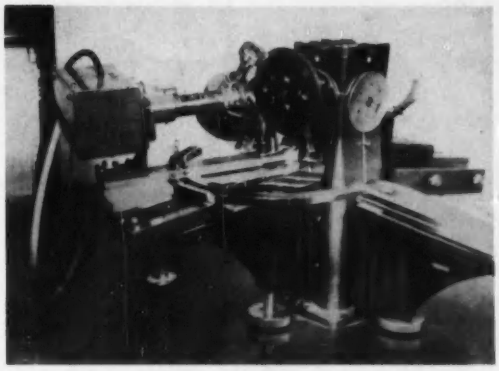

Fig. 4. Geiger counter diffractometer for measurement of crystallite orientation in fibers.

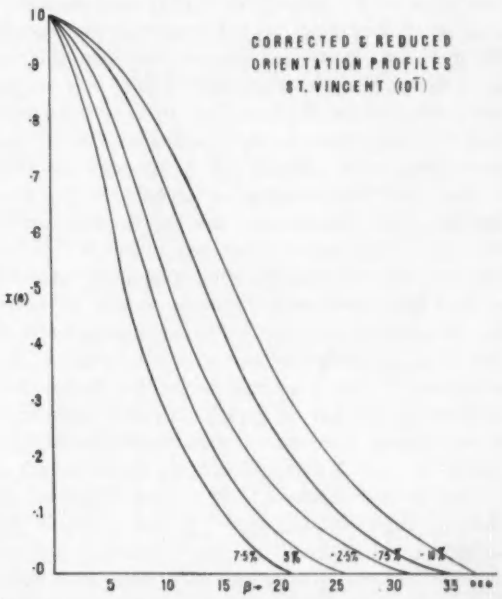

Fig. 5. Corrected and reduced azimuth scans of (10$\bar{1}$) diffraction profile of St. Vincent cotton mercerized at various stretches.

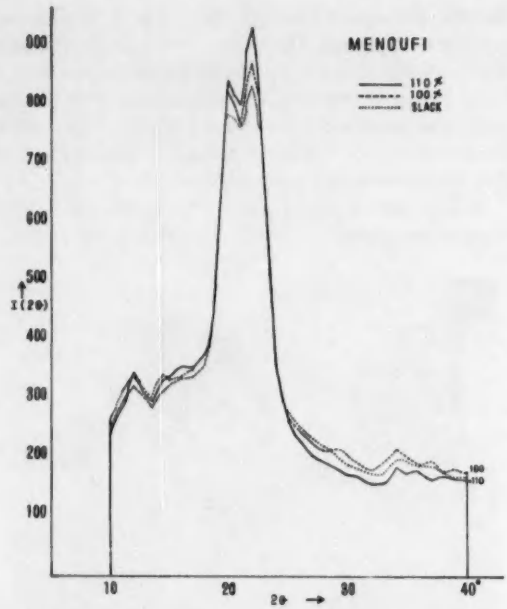

Fig. 6. Radial scan of x-ray diffraction by Menoufi cotton mercerized at different stretches. The 100% has been stretched to the original dry length.

tion factor. The subtracted "background intensity" consists of scattering by noncrystalline material in the specimen, incoherent scatter, and scattering by air in the path of the transmitted beam. Air scatter was minimized by the use of an efficient beam stop mounted very close to the specimen. There was some difficulty in judging the background intensity of the $(10\bar{1})$ interference on account of the fact that the (021) interference also appeared at nearly the same Bragg angle and an azimuth of 60° or so. However, the two profiles were completely resolved at the higher stretches. A more serious difficulty was encountered with the (101) interference, which showed a gradually trailing tail rather than a flat background. It was not easy to decide whether this tail actually belonged to very disoriented crystallites or was caused by oriented noncrystalline material. Finally, it was also not possible to decide whether the background intensity, which was measured at relatively high latitude angles β and γ, could be justifiably extrapolated to the equatorial region. Answers to some of these questions could have been obtained by using a diffractometer with a high radial and angular resolution and crystal-monochromatized rather than filtered radiation. In the present study, these refinements were not considered necessary, since the orientation factors were determined with an estimated precision of ± 0.01, which was considered adequate.

In the case of unmercerized cottons, the crystallite orientation factor was solely determined from the intense (002) interference according to the formula [10]

$$F(x) = 1 - \tfrac{3}{2}\,\overline{\sin^2 \delta} \qquad (3)$$

Here δ is the azimuth angle of the (002) interference and $\overline{\sin^2 \delta}$ is defined similarly to $\overline{\sin^2 \beta}$ and $\overline{\sin^2 \gamma}$.

Estimates of Crystallinity

It is known that the crystallinity of cotton decreases from 70% to 50% when the fiber is thoroughly mercerized [6]. However, there seem to be no detailed studies relating to the effect of mercerizing stretch on crystallinity. X-ray methods of measuring fiber crystallinity make use of "radial scans" of intensity scattered by the disoriented fiber at various angles. The crystallinity can be calculated by comparing the total intensity of diffraction under crystalline peaks with the maximum intensity of scattering in the amorphous region, after corrections have been made for air scatter, incoherent scatter, absorption by the specimen, etc. [6]. Crystallinity can also be estimated by trying to compound the radial scan curve of the sample from the curves for a crystalline and an amorphous standard [16]. The radial scans of Menoufi fibers, mercerized slack and also stretched to 0% and 10%, are shown in Figure 6. These curves were obtained by a point-to-point scan using the Philips x-ray diffractometer. The diffractometer employs a focusing geometry which requires wide, flat specimens. Such specimens were prepared by cutting the fibers into small fragments (below 1 mm. in length), loading them into the specimen holder, and flattening the face exposed to the x-ray beam. This procedure was also essential in order to minimize the effects of preferred orientation in the fiber.

By comparison of the diffraction chart of raw cotton obtained on this instrument with previous published records [16], it was verified that this technique of specimen preparation effectively randomized the effects of preferred orientation.

The curves have been normalized by dividing the scattered intensity at each angle by the area of the angle versus intensity curve. Corrections (for

counter dead time, air scatter, instrument geometry, etc.) have not been applied, as they were thought to be unnecessary [16]. From the curves, it will be seen that there is a slight but by no means serious increase in crystallinity with increasing stretch. Since the effect was found to be so slight, it was not thought worthwhile to make full computations of crystallinity.

The Measurement of Tensile Properties

Since the fibers were mercerized and their x-ray diffraction studied in bundle form, it was decided that tensile measurements could also best be made on bundles. The Stelometer [7] was used for obtaining values of bundle breaking length at 0 and $\frac{1}{8}$-in. test lengths as well as the bundle extensibility at the latter test length. Some measurements were also made on single fibers at 1-cm. test length with the Instron tensile tester. The estimated precision in these measurements was ± 2 Km. for bundle breaking length and ± 0.5 g. for single fiber strength. These values are somewhat poorer than the precision obtained in ordinary cotton testing on account of the limited sample size and the extra variability introduced by the mercerizing process.

Results and Discussion

The relevant properties of the raw cottons studied are listed in Table I, along with the initials used for identifying the cottons in later references and figures.

On mercerization, all these cottons increased in orientation, as shown in Figure 7. It was clear that the increase was connected with the original orientation of the cottons, as shown in Figure 8, which shows the orientation factors for raw fibers and for fibers mercerized with restretching to their original lengths.

With all the cottons studied, the mercerizing treatment has been found to increase the fiber orientation, even when the cottons are allowed to contract freely during swelling and washing. This will be clear from a comparison of the spread of the (002) diffraction arcs for raw and slack mercerized fibers, as shown in Figure 3, and even more surely from a comparison of the f_x values reported in Tables I and II. It is known that in the case of fibers like ramie and jute, slack mercerization *decreases* the orientation. Cotton seems to show a contrary behavior, which may be due to the partial straightening of the convoluted fiber during swelling [9]. Such a deconvolution would align the axes of fibrils more nearly parallel to the fiber axis. When the spiral angle is not pronounced, as in ramie, jute, or flax,

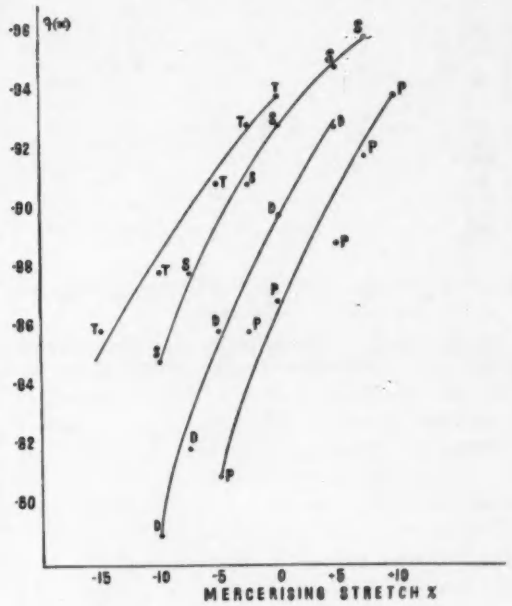

Fig. 7. Relation between orientation and mercerizing stretch.

TABLE I. Some Properties of Raw Cottons Studied

Fiber property		Triple hybrid T	St. Vincent S	Menoufi M	Giza G	Deltapine D	Pima P
X-ray orientation factor f_x		0.83	0.79	0.77	0.76	0.74	0.69
Bundle breaking length, Km. (B. L.)	0	42	41	44	39	31	—
	⅛ in.	24	26	25	21	18	—
Bundle extension at ⅛ in. test length (E%)		4	4	8	6	5.5	—

the net effect of an intracrystalline swelling agent would, however, be to disorient the molecular chains with respect to the fibrillar axes, or what is nearly the same, the fiber axis.

Figures 9 and 10 show some of the tensile test results on the mercerized cottons. It is seen that different cottons show specific relations between tensile strength and mercerizing stretch and that these relations exhibit a striking similarity to the relations between orientation and mercerizing stretch shown in Figure 7. In fact, it looks as though there may be a common relation between orientation and bundle breaking length for all the mercerized cottons studied. That this is indeed the case is shown in Figure 11.

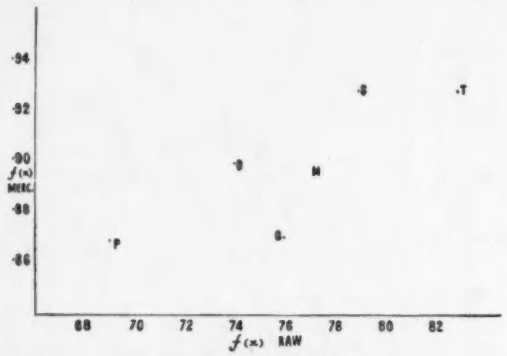

Fig. 8. Change in orientation caused by mercerizing with restoration to original length.

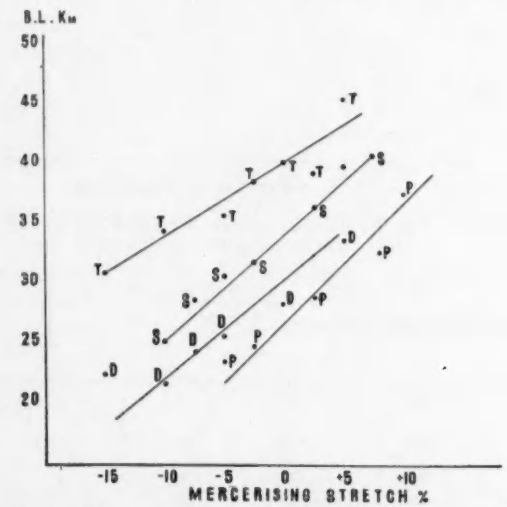

Fig. 9. Effect of mercerizing stretch on bundle breaking length of mercerized cottons at ⅛-in. test length.

Figure 11 shows the breaking length data for all the cottons studied in this series at two test lengths. All the cottons, except the Triple Hybrid series, show uniform scatter around a common line. The lines for the two test lengths seem to be roughly parallel. These lines were drawn by inspection. Second degree curves were also analytically fitted to the data, but found to give a slightly poorer fit than the lines drawn by inspection. Nevertheless, the second degree line would explain 90% of the variance in strength of the pooled data for all cottons, with the exception of the Triple Hybrid series. The curves drawn by inspection should give an even better fit.

It is interesting to compare the above situation with the extensive data available for unmercerized cottons [2, 10, 11]. These data can be summarized as follows.

1. At zero test length, there is a linear (negative) correlation between bundle strength and x-ray angle ($r = 0.75$). The situation becomes better when orientation factors are used instead of x-ray angles ($r = 0.84$). When cottons are separated into their botanical species, the correlation within any one species can become as high as 0.90.

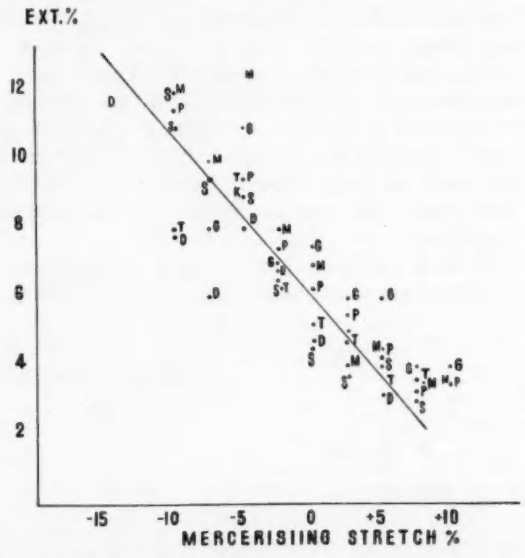

Fig. 10. Effect of mercerizing stretch on bundle extensibility of mercerized cottons at ⅛-in. test length.

TABLE II. Some Properties of Slack Mercerized Cottons Studied

Fiber property		Triple hybrid T	St. Vincent S	Menoufi M	Giza G	Deltapine D	Pima P
X-ray orientation factor f_x		0.86	0.85	0.82	0.80	0.75	—
Bundle breaking length, (B. L.), Km.	0	35	26	27	25	29	27
	⅛ in.	31	25	23	21	23	27

2. When the bundle test length increases, correlations between bundle strength and orientation become progressively poorer, owing to the larger effect played by "weak links" on bundle strength. A recently published report [11] on 16 cottons (mostly American Uplands) has listed the strength versus x-ray angle correlation coefficient as −0.92, −0.70, and −0.39 at test lengths of 0, 1.5, and 5 mm. respectively. These figures would assign a value of −0.54 for the correlation at a test length of ⅛-in.

The present data on mercerized fibers show some striking differences from the above picture for unmercerized fibers. In the first place, the relation between strength and orientation is definitely nonlinear. Second, the correlation between strength and orientation is quite strong even at ⅛-in. test length, even when different cottons are considered. The mercerizing process thus appears to diminish the effect of weak links. Of course, this is not a very sound conclusion unless it is supported by data pertaining to a much larger number of cottons than now studied and belonging to all the botanical species. If such data show that the correlation between bundle strength and orientation factor at high test lengths is improved by mercerization, then it becomes clear that mercerization can partially reduce the difference between "substance strength" and the strength of weak links.

A much stronger clue about the effect of mercerization on weak links is afforded by a comparison of the strengths of unmercerized and "slack mercerized" fibers, as reported in Tables I and II.

Slack mercerization is seen to diminish the strength at zero test length, but to leave the strength at ⅛-in. largely unaltered. The diminution at zero test length results from decreased crystallinity, which swamps the effect of the small increase in orientation. If mercerization caused no other changes in the fiber, the strength at ⅛-in. test length should also have been correspondingly diminished. There being no such diminution, one has to conclude that the

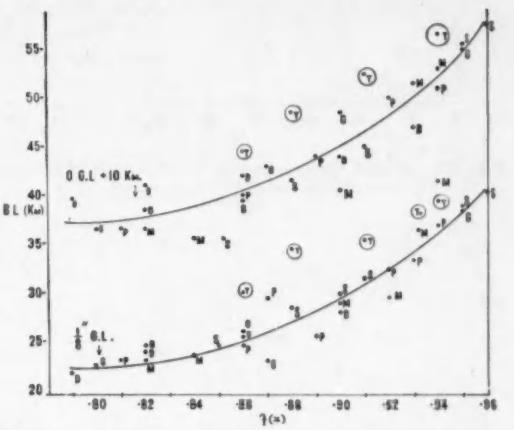

Fig. 11. Relation between crystallite orientation and bundle strength of mercerized cottons.

change in crystallinity does not affect the strength of the weak links, or probably even increases their strength. It would be plausible to assume that the weak links are built-in strains during the growth of the fiber and that some of the strain can be eliminated by a strong swelling treatment. More information on this point can be obtained by obtaining the complete curves of strength versus test length on single fibers as well as bundles before and after mercerization. Single fiber tests are necessary because in bundle tests one cannot pin down the effects of strength and extensibility separately. Some single fiber studies have recently been reported for jute and ramie with much the same objectives in mind [1].

Passing now to the data on bundle extensibility, it will be seen from Figure 10 that the effect of mercerizing stretch seems to be described, though with a good deal of scatter, by one common straight line for all cottons. The relation between extensibility and orientation factor is also linear, as seen from Figure 12, but apparently different cottons plot

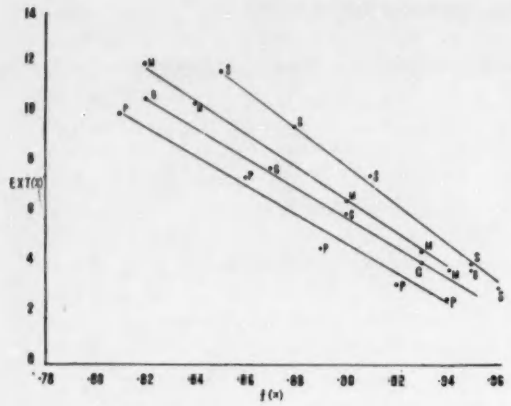

Fig. 12. Relation between crystallite orientation and bundle extensibility of mercerized cottons.

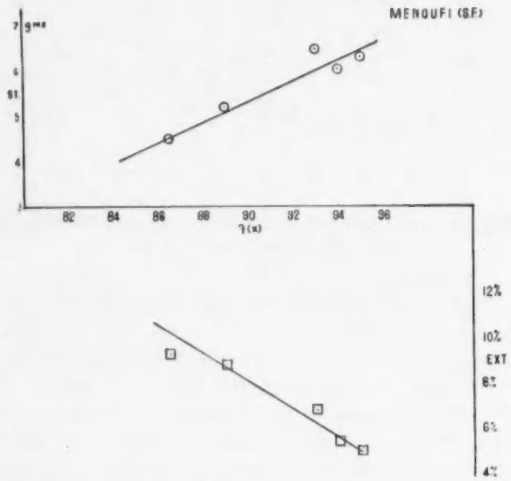

Fig. 13. Effect of orientation on single fiber tensile properties of mercerized Menoufi cotton.

on different straight lines with a common slope. Nevertheless, a single straight line can still be fitted to these data with as high a correlation as −0.82 as against a reported correlation [7] of 0.66 between bundle extensibilities and x-ray angles of raw cotton. Since the Stelometer is not a very accurate instrument for measuring bundle extensibility, which is itself a rather complicated effect, too much meaning should not be read into these data. The important thing to note is that large decreases in extensibility can be caused by relatively small increases in orientation factor. It is also worth while to notice that the process of slack mercerization can almost double the extensibility of the raw fiber.

Figure 13 shows the effect of mercerization on strength and extensibility of single fibers of Menoufi cotton, tested at 1-cm. length. The data are averages for 100 fibers. Both strength and extensibility appear to vary linearly with orientation factor. Since the fiber becomes finer at higher mercerizing stretches, which cause high orientation factors, the relation between breaking length and orientation would again be curvilinear, as in Figure 11.

Conclusions

1. The length contraction of cotton fiber bundles when swollen with caustic soda of mercerizing strength is of the order of 10–15%, and the swollen fibers can be restretched to about 10% in excess of their dry length and washed under stretch without breaking the fibers.

2. The crystallite orientation factor of fibers mercerized in the above manner can range from below 0.80 to above 0.95, depending on the mercerizing stretch and on the orientation of the unmercerized fiber. Mercerization, even under free shrinkage, increases fiber orientation.

3. The crystallinity of the fiber, which is known to decrease during mercerization, tends to recover slightly at high mercerizing stretch.

4. After slack mercerization, the effect of test length on fiber bundle strength is somewhat different from the case of unmercerized fibers. The difference suggests that the weak links in the fiber become relatively less weak after the strong swelling treatment, compared to the "fiber substance," which diminishes in strength on account of diminished crystallinity.

5. The breaking length increases with orientation in a nonlinear manner. The relationship is quantitatively much the same for mercerized cottons belonging to different varieties.

6. The effect of crystallite orientation on extensibility at break is very strong, though it is specific for each type of cotton.[1]

[1] After the above paper was written, some new work has appeared on "Mechanical Properties of Cotton Fibers and Their Response to Mercerization" (L. Rebenfeld, TEXTILE RESEARCH JOURNAL **28**, 462, 1958). Working with different cottons, Rebenfeld has attempted to correlate the fiber orientation (or rather, initial Young's modulus) *prior to mercerization* with the relative changes in mechanical prop-

Acknowledgments

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erties caused by mercerization. The fiber mercerization has been carried out at controlled tension and not controlled extension. It will be seen that the present paper, though dealing with the same subject, has used a different approach. Thus the conclusions set forth in the two papers, which at first sight seem to disagree on some points, are in fact not directly comparable.

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Some Observations on the Vibration and Whirling of Continuously Loaded Spindles

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Abstract

Formulas are derived for the frequency of flexural vibration of a vertical uniformly tapered circular shaft mounted at one end. The Rayleigh and Dunkerley methods are used and the results compared both with known results of exact analysis and with experiment.

On the basis of an extension of Dunkerley's principle, a simple formula is derived for the effect of the mass of a textile package on the critical speed of a vertical shaft held at its base.

Introduction

The study of mechanical vibration is important in many branches of the textile industry. In spinning, however, it assumes an increased importance owing to the delicate nature of the product. Two main types of vibration can cause the quality of the yarn spun to drop: torsional vibration in the feed rollers and whirling of the spindle blades themselves. The purpose of this paper is to discuss the flexural

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vibration and whirling speeds of spindle blades; The application of such studies to commercial textile spindles is illustrated by a typical example.

Theoretical Background

The frequencies of flexural vibration can be calculated accurately for simple shapes with known mountings. Two examples are relevant here: (a) For a cylindrical shaft rigidly fixed at one end, the exact analysis is well known and the solution of the differential equation presents no difficulty [13]. Second order effects such as shear and rotary inertia are either known or can be estimated. (b) Kirchhoff has treated the sharp-pointed shaft analytically [13, 14].

It is difficult and complicated to obtain analytical solutions for complex shapes. There are, however, two approximate methods of calculation which are useful: Rayleigh's energy method (and its extension, the Rayleigh-Ritz method) and the extension of Dunkerley's formula for the whirling speed of a shaft carrying several rotors.

Experimental Background

Some theoretical and practical aspects of shaft whirling have been discussed by Downham [3] in a series of papers on the subject. A symmetrical rotor on a shaft is made to simulate an aircraft propeller blade; consequently, the moment of inertia of the system about the axis of the shaft is large. With textile spindles, however, the opposite is the case; the moment of inertia about the axis being small, the system consists essentially of a continuously loaded vertical cantilever. The experimental techniques are similar in the two cases, however.

Johnson [6] gives the general equation for rotational and vibrational frequencies of elastic bodies.

Püschmann [10] has discussed the effect of the shaft mounting on the frequency of vibration; i.e., an "end effect." Cranch and Adler [2] give frequency equations for several cantilever shafts closely allied to the ones discussed here.

Scope of Present Work

Formulas have been derived for the flexural vibration and critical speeds of uniformly tapered spindles by Rayleigh's method and by Dunkerley's method. All these methods are approximations, since they either impose artificial restrictions on the degrees of freedom available, restrictions which do not in fact exist, or neglect to take into account some restrictions which do exist. To check the degree of approximation attained, the solutions obtained by each method for right circular cylinders and for sharp-pointed shafts are compared with the exact solutions already known for these two shapes. In choosing or rejecting a method of calculation, each method is judged according to the degree of approximation attained and also according to the complexity involved in the calculation.

Finally, the theoretical results are compared with experimental data on shafts of different forms.

TABLE I.

Shape	σ_R(Rayleigh)	Corresponding factor in exact analysis
Cylindrical shaft	0.8825	0.8790
Sharp-pointed shaft	2.600	2.180

Theoretical Treatment

Rayleigh's Method

Figure 1 depicts a uniformly tapered shaft of length L and circular in cross section. One end of the shaft is rigidly built into a massive support. In Appendix I is given the detailed derivation of the fundamental frequency of flexural vibration using Rayleigh's method; the meaning of all the symbols used is given on page 333. The result is

$$\omega = 2\pi\nu = \sigma_R \left(\frac{D_2}{L^2}\right)\sqrt{\frac{Eg}{\gamma}} \qquad (1)$$

where

$$\begin{aligned} 16\sigma_R^2 = {} & \left[28.80\left(\frac{D_1}{D_2}\right)^4 + 96.00\left(\frac{D_1}{D_2}\right)^3\left(1-\frac{D_1}{D_2}\right)\right. \\ & + 123.43\left(\frac{D_1}{D_2}\right)^2\left(1-\frac{D_1}{D_2}\right)^2 + 72.00\left(\frac{D_1}{D_2}\right) \\ & \left.\times\left(1-\frac{D_1}{D_2}\right)^3 + 16.00\left(1-\frac{D_1}{D_2}\right)^4\right] \\ & \div\left[2.3111\left(\frac{D_1}{D_2}\right)^2 + 0.9143\left(\frac{D_1}{D_2}\right)\right. \\ & \left.\times\left(1-\frac{D_1}{D_2}\right) + 0.1481\left(1-\frac{D_1}{D_2}\right)^2\right] \qquad (2) \end{aligned}$$

and σ_R is a shape factor depending upon the taper of the shaft. Table I gives a comparison of the results of Equation 1 with the known analytical results for cylindrical and sharp-pointed shafts.

Hence, Rayleigh's method gives a general formula which is 0.4% too high for cylindrical shafts and 19% too high for sharp-pointed shafts. The accuracy for cylindrical shafts is extremely good, but unfortunately the error of 19% for sharp-pointed shafts is excessive. Furthermore, physical considerations would lead to the belief that σ_R should tend to zero as D_2 approaches zero, whereas Equation 1 does not give this result. In the case of the sharp-pointed shaft, direct application of Ray-

Nomenclature

Symbol	Definition	Unit
a, b, c	constants defined in the text	dimensionless
A_x	area of cross section of shaft at point x	in.^{2}
D_1	diameter of free end of shaft	in.
D_2	diameter of fixed end of shaft	in.
D_b	diameter of base of tube carrying yarn	in.
D_s	diameter of textile spindle blade	in.
D_t	diameter of tube carrying yarn	in.
D^*	maximum depth of yarn on tube	in.
E	Young's modulus of material of shaft	lb./in.^{2}
F	force applied at free end of a light shaft in static case	lb.
g	acceleration due to gravity	in./min.^{2}
I_x	moment of inertia of a cross section perpendicular to the axis at point x	in.^{4}
L	length of shaft (or shaft blade)	in.
N	number of segments in interrupter disc	dimensionless
R	angular velocity of interrupter disc	r.p.m.
T_m	maximum kinetic energy of shaft	in.-lb.
t	time coordinate	min.
V_m	maximum potential energy of shaft	in.-lb.
x	distance along shaft measured from a particular end	in.
X	space part or "form" of displaced shaft	in.
$y = X \sin \omega t$	displacement of shaft at a typical point along it	in.
Y	ordinate for yarn profile	in.
ξ_1, ξ_2, ξ_3	functions of (λ/L) defined in text	dimensionless
γ	density of material of shaft	lb./in.^{3}
γ_s	density of spindle blade	lb./in.^{3}
γ_t	density of tube carrying yarn	lb./in.^{3}
γ_y	density of yarn	lb./in.^{3}
Δ	deflection at tip of shaft in static case	in.
κ ($\leqslant 1$)	ratio $\frac{\text{rotational critical speed}}{\text{frequency in A.C. bearings}}$	dimensionless
λ	length of base of tube carrying yarn	in.
μ_x	force per unit deflection at point x of shaft	lb./in.
ν	frequency of vibration	r.p.m.
$\nu_{R\theta}$	frequency of shaft in a perfectly rigid mounting	r.p.m.
$\nu_{B\theta}$	frequency of shaft in angular contact bearings	r.p.m.
σ_R, σ_D	functions of D_1/D_2 occurring in Rayleigh and Dunkerley calculations respectively	dimensionless
$\tilde{\sigma}$	for shaft is equal to $\omega L^2 \sqrt{\frac{\gamma}{Eg}}$	in.
τ	period of vibrations	min.
χ ($\leqslant 1$)	ratio $\frac{\text{frequency in A.C. bearings}}{\text{frequency in rigid mounting}}$	dimensionless
ω	circular frequency	radian/min.
Ω	angular velocity	r.p.m.
Ω_c	critical rotational speed	r.p.m.

leigh's method gives a frequency 5% higher than Kirchhoff's value (the trial functions being different in the direct and general methods owing to the boundary conditions).

Finally, it is obvious that the method is simple for particular cases such as the cylindrical or sharp-pointed shaft but appears to be intrinsically cumbersome for the intermediate case of a truncated cone.

Rayleigh-Ritz Modification

Little was gained in accuracy by using one of the simplest forms of Ritz modification to Rayleigh's method. The formulas became excessively complicated; consequently it was not thought worth while to proceed further.

Application of Dunkerley's Principle

Dunkerley [4] formulated an empirical rule for the whirling speed of a light shaft carrying several rotors. If ω_i denotes the whirling speed of the shaft when carrying the ith rotor alone, then the whirling speed when carrying a series of rotors is given by

$$\frac{1}{\omega^2} = \sum \frac{1}{\omega_i^2} \tag{3}$$

For adding a series of masses to a spiral spring, for example, it is true that the resultant period of vibration is given by the following (Equation 4)

$$\tau^2 = \sum \tau_i^2 \tag{4}$$

This principle is used here to calculate the period of vibration of a uniformly tapered shaft, the summation being replaced by an integration for a series of infinitely thin discs.

Details of the calculation are set out in Appendix II. The result is

$$\omega = 2\pi\nu = \sigma_D\, 0.8661 \left(\frac{D_2}{L^2}\right)\sqrt{\frac{Eg}{\gamma}} \tag{5}$$

where σ_D is a shape factor given by

$$\sigma_D^2 = \frac{5}{1 + 4\left(\frac{D_1}{D_2}\right)} \tag{6}$$

Table II gives a comparison of the results obtained by Equation 5 with known analytical results for cylindrical and sharp-pointed shafts.

Hence, the application of Dunkerley's principle gives a general formula which is 1.5% low for cylindrical shafts and 11% low for sharp-pointed shafts.

This formula is very simple and easily adaptable to slide rule calculations. The maximum error of

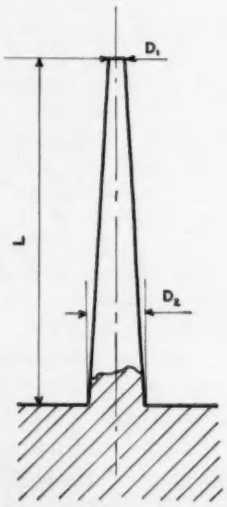

Fig. 1. Uniformly tapered shaft built in at one end.

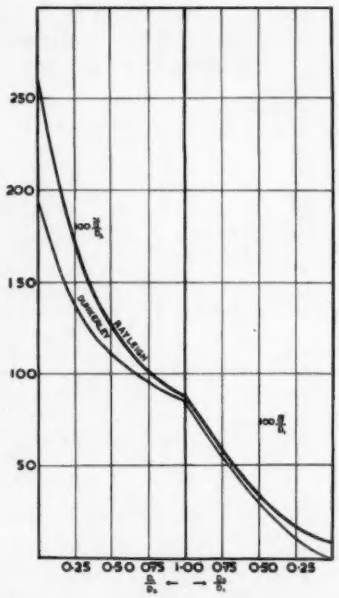

Fig. 2. Calculated values of $\tilde{\sigma}$ where $2\pi\nu = \tilde{\sigma}/L^2\sqrt{Eg/\gamma}$.

TABLE II

Shape	$0.8661\ \sigma_D$ (Dunkerley)	Corresponding factor in exact analysis
Cylindrical shaft	0.8661	0.8790
Sharp-pointed shaft	1.936	2.180

11% is rather better than 19%. Finally, Equation 5 gives $\omega \to 0$ as $D_2 \to 0$ which physical considerations would lead us to expect, since the shaft would merely topple over.

Although Equation 4 is true for a series of masses on a spring, it does not necessarily follow that it is true for shafts since the addition of masses at different parts of the shaft might conceivably modify its elastic properties [1]. This discrepancy might apply even more to a series of discs of varying diameters (tapered shaft) than to a series of uniform ones (cylindrical shaft) and therefore result in a bigger error for sharp-pointed than for cylindrical shafts.

When the frequency is expressed in the form

$$\omega = 2\pi\nu = \bar{\sigma}\,\frac{1}{L^2}\sqrt{\frac{Eg}{\gamma}} \qquad (7)$$

Figure 2 gives curves enabling $\bar{\sigma}$ to be found for the Rayleigh and Dunkerley cases if the value of (D_1/D_2) is known.

General Remarks

When the dimensions of the shaft are of the same order as those of textile spindles, the effect of rotary inertia is negligibly small [11].

The effect of shear is also negligibly small [13]. This is also confirmed by the fact that for a steel cylindrical shaft $10 \times \frac{1}{2}$ in., for example, allowed to deflect under its own weight, the static deflection due to shear is negligible compared to that due to bending [12].

The theoretical treatment given above applies strictly only to flexural vibrations. When a shaft is rotating with an angular velocity Ω, the frequency of transverse vibration ν is different from the natural frequency ν_0 of the shaft when not rotating. This difference depends on the moment of inertia of the shaft in addition to the angular velocity. The theory of this was first discussed by Chree [1] in 1904, the modern viewpoint being given by Green [5]. (See also Johnson [6] for the general equations.)

TABLE III

Shaft	Type	L, in.	D_1, in.	D_2, in.
1	inverted taper	10	1	1/2
2	inverted taper	10	2/3	1/2
3	cylindrical	10	1/2	1/2
4	normal taper	10	3/8	1/2
5	normal taper	10	1/4	1/2
6	normal taper	10	1/8	1/2

The effect of viscous (air) drag on the rotating shaft is negligibly small compared with the effect of centrifugal force [7].

For a steel shaft $10 \times \frac{1}{2}$ in., the natural frequency of torsional oscillation is approximately 5×10^6 r.p.m. Hence, transient and natural torsional oscillations are unlikely to play any part in the present investigations, where the frequencies encountered are of the order of thousands of revolutions per minute.

The theoretical treatment above supposes that the shaft is rigidly mounted in an infinitely massive base. In practice, the mountings may have energy dissipating properties; i.e., could act as mechanical impedances. More particularly in spinning frame spindles, the mounting is not rigid and the question of bearing clearances becomes important.

The authors are indebted to Professor R. C. Johnson for pointing out that if the shaft is running in a bearing with clearance, then at the whirling speed, one particular point on the shaft should remain in contact with the bearing. Although the amplitude of whirl at a particular speed will be larger, the speed at which maximum deflection occurs should be unaffected by clearance.

Flexural vibration with clearance presents a somewhat different problem from that of shaft whirling. As it is relatively unimportant compared with shaft whirling in textile spindles, the theory is not discussed here.

Experimental Work

A practical division of the experimental work into frequencies of flexural vibration and critical rotational speeds was made. In Figure 3 the design of the spindles used is illustrated. Table III gives the dimensions and type of the spindles used. The shaft length L was measured from the tip of the shaft to the top of the flange F. The shaft, flange, and insert (or base) I were machined in one piece. Figure 3 shows the shafts held in a sleeve (or muff)

S which was used only when a shaft was held in bearings. This sleeve was ground internally and an accurate push-fit obtained and then secured by a bolt and washer, the bolt screwing into the base of the shaft itself.

For the study of flexural vibrations, the shafts were mounted in bearings in one series of experiments, in a lathe-chuck in a second series, and embedded in concrete in a final series. The rotational experiments were done first, since once the shaft was embedded in concrete or gripped by chuck jaws, the carefully machined surface would be damaged. But it will be more helpful in following this paper to describe the work on flexural vibration with concrete mounting first, even though the actual order of procedure was (a) rotation and measurement of critical speeds, (b) flexural vibrations of shafts held by sleeve in angular contact bearings, (c) flexural vibrations of shafts gripped in a lathe-chuck, and (d) flexural vibrations of shafts embedded in concrete.

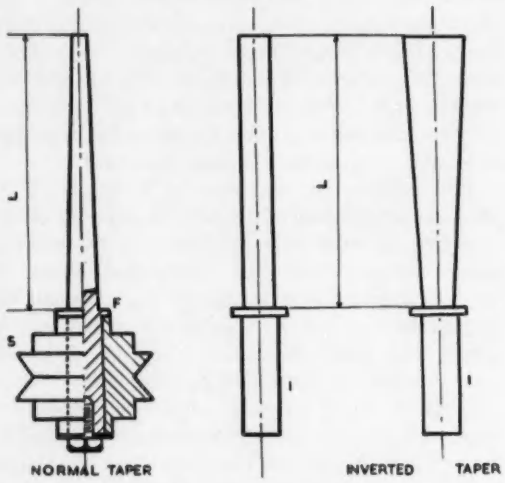

Fig. 3. Design of shafts.

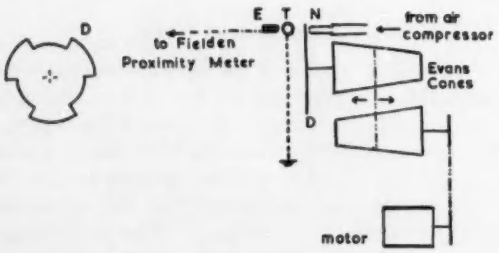

Fig. 4. Apparatus used for investigation of flexural vibrations.

Flexural Vibrations

Mild steel shafts of different shapes were examined. Compressed air was used as a means of exciting the shafts into vibration, the excitation frequency corresponding to resonance being taken as the natural frequency of the shaft. The shaft was excited by directing a jet of air from a nozzle N onto the tip of the shaft T. Figure 4 shows that the stream of air was interrupted by a disc D from which a number of segments had been cut out.

If the number of segments removed from the disc is N and the angular velocity of the disc is R r.p.m., the number of impulses delivered to the tip of the shaft per minute

$$\text{Imp}_{\text{min.}} = N \times R \qquad (8)$$

The excitation frequency of the air jet could be varied continuously simply by varying R. The disc was attached to the output shaft of a pair of cones, the input shaft being driven at a constant speed by a three-phase electric motor. Both the motor and the base plate of the cones were securely bolted to the same large block of concrete. This helped to reduce the amount of unwanted vibration (see also *Critical Rotation Speeds*).

Various mountings were used. (a) The shafts were examined in the mounting used for the rotational experiments (the shaft and sleeve as a unit

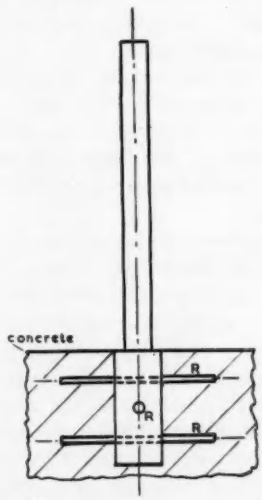

Fig. 5. Rigidly mounted shaft.

were held in bearings), (b) the shafts were gripped in the jaws of a lathe-chuck, the chuck itself (average weight 37 lb.) being supported on a block of cast iron, or (c) rigid mounting (the shafts were embedded in concrete). Each shaft was isolated from the other and reinforced in position by three steel rods R (1/8-in. diameter and about 4 in. long) passed through the insert, the middle one being at right angles to the other two (Figure 5).

With cylindrical and normal taper shafts it was possible to isolate three or four shafts in the same block of concrete. With the two heaviest shafts, i.e., the ones of inverted taper with $D_1 > D_2$, it was necessary to use separate and more massive blocks to get consistent results with sharp resonance points.

Finally, the case of three shafts of different materials coupled by a $\frac{1}{2}$-in. steel plate was examined. The steel plate rested on top of the concrete, the shaft inserts being pressed through holes in the plate as shown in Figure 6.

For the above experiments, the blocks of concrete were supported on three (or four) small carefully adjusted steel jacks with pointed tips. Supporting the concrete blocks on three points helped to eliminate most of the unwanted vibration being transmitted to the shaft.

To detect vibrations in the shaft, a Fielden Proximity Meter, Type PM2, was used. The electrode E in Figure 4 was placed close to the tip T of the shaft, the shaft itself being earthed. Small displacements of T resulted in changes in electrical capacitance between E and T, and a capacitance-sensitive circuit converted these changes into varying electrical potentials which could be displayed on an oscillograph screen. In the Proximity Meter, a 3Kc/sec. carrier wave was modulated by the capacitance changes and the modulated output taken onto the oscillograph plates. As the frequency of excitation of the shaft was varied, the envelope of the carrier wave broke up into a series of peaks and then became uniform again. The point of maximum modulation was taken as the resonance point of the shaft.

The use of the Proximity Meter in examining the transverse vibration of rods and reeds is discussed in a paper by Kirby [7].

To check the accuracy of the method, a standard C 256 tuning fork was substituted for the shaft and the point of resonance found by means of the technique described above. The measured value of the natural frequency of the fork was found to be correct

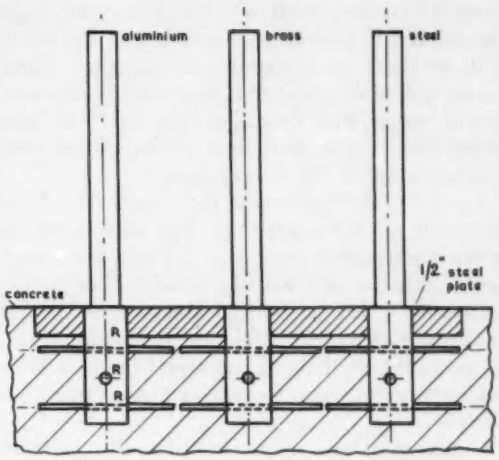

Fig. 6. Shafts rigidly mounted and coupled by a steel plate.

to 0.5%. The speed of the interrupter disc itself (in the air stream) was measured by means of a "Strobotorch" which had previously been calibrated against the mains supply. The frequency of the mains at the time of calibration was ascertained from the Electricity Board.

Critical Rotational Speeds

The bases of the shafts were all accurately machined to obtain a good push-fit into the sleeve, sleeve plus shaft being allowed to rotate in self-aligning bearings. The bearing housing unit was bolted to a steel plate which was embedded in a massive block of concrete.

The system was self-exciting. As the speed was increased, the shaft began to whip as the critical speed was approached. For critical speeds below about 8000 r.p.m., it was possible to run the shaft quickly through its critical point. Protection was provided by placing a cylindrical guard round the shaft of the same length as the shaft itself. This steel cylinder was bolted to the bearing housing unit. This was necessary when the shaft was passing through its critical speed; in one instance the vibrations could be felt two rooms away from the laboratory.

An optical means of measurement was considered to be the simplest and most practical here [8]. A small ball bearing B was attached by "Bostick" to the tip of the shaft (see Figure 7). This was illuminated by light from a condenser unit C. A lens

L enabled an image of B to be obtained on a ground glass screen G placed vertically above the shaft. With the shaft stationary or rotating at low speed, a small spot of light could be observed on the screen. As the speed was increased, however, the spot turned into a circle, the diameter of which increased to a maximum at the critical speed.

A graph of the diameter of the image of B against rotational speed was plotted. The position of the asymptote was estimated and taken as the experimental value of the whirling speed. In some experiments, it was possible to obtain experimental points both above and below the critical speed; i.e., the asymptote could be approached from both sides and consequently its position estimated more accurately.

The same mounting was used for all rotational experiments. Self-aligning bearings were used because (a) it was easier to assemble the unit when using this type of bearing than with other types, (b) it was thought that there would be less likelihood of damage to the actual bearings themselves as the critical speed was being passed through, and (c) possibly a greater measure of safety was afforded to personnel. The rotational experiments being completed, the self-aligning bearings were replaced by the angular contact type. Repeating the safer rotational experiments showed that the critical speed was not affected, although sharper definition of the resonance peak was obtained.

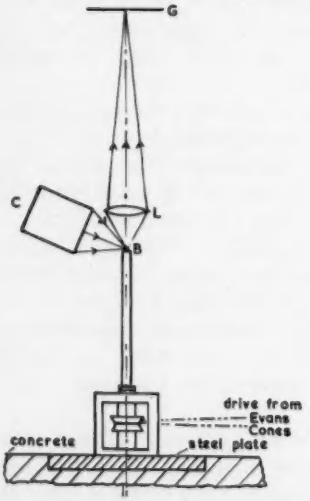

Fig. 7. Apparatus for determination of whirling speeds.

To check the possibility of unwanted vibrations being transmitted to the shaft from the cones, a flywheel was attached to the output shaft of the cones. This flywheel was $6 \times \frac{1}{2}$ in.; its moment of inertia about the axis of the output shaft was 1.75 times that of one of the cones itself. Experiment showed that this had no significant effect on the resonance curves.

When a single- instead of a three-phase motor was used, the definition of resonance was slightly worse. No significant change in the position of the resonance peak was observed.

Results

Cylindrical Shafts

With a shaft embedded in concrete, six pairs of readings of the resonance frequency were taken. A pair of readings constituted a twofold determination of the resonance point by approaching it from both below and above its natural frequency. Three experiments were carried out with each shaft, making a total of 36 readings (18 pairs) for each mean. Table IV gives the mean experimental frequencies of three mild steel shafts isolated in concrete and the corresponding theoretical frequencies. The bases of these three particular shafts were left unmachined and consisted of 1×4 in. steel bars. This was done to achieve absolute rigidity in order to get agreement between experiment and exact analysis. Theory and experiment agree here, the difference being less than the order of experimental error.

Table V gives the experimental results when three shafts of different materials were coupled by a steel plate.

The resonance frequencies were deduced in a similar manner when using the other mountings.

When the shaft was mounted in angular contact bearings, however, the resonance peak was very broad. A pair of readings constituted the point where resonance started when approaching resonance from below and the point where resonance started when approaching resonance from above. The average was taken as the resonance frequency in a particular experiment.

Critical rotational speeds were estimated by plotting the amplitude of whirl against speed of rotation. When it was possible to approach the critical speed from above and below, both branches of the amplitude–speed curve could be plotted. With a complete curve, the position of the asymp-

TABLE IV

Dimensions, in.	Natural frequency in rigid mounting, r.p.m.	Theoretical frequency, r.p.m.
0.14 × 10	2,340	2,350
0.25 × 10	4,170	4,190
0.50 × 10	8,380	8,380

TABLE V*

Dimensions, in.	Material	Observed frequency, r.p.m.	Theoretical frequency, r.p.m.†
1/2 × 10	mild steel	8,200	8,380
5/8 × 10	brass	6,800	7,150
1/2 × 7.4	aluminium	15,000	15,600

* See also Table VII.

† The modulus of elasticity for mild steel was taken as the mean of nine dynamic determinations with C.V. of 1%. With the less elastic brass and aluminium, however, the modulus was deduced from load–extension curves.

tote could be ascertained without ambiguity. Four of these graphs were obtained for each shaft, and the average whirling point taken as the observed critical speed.

With the shafts of normal taper, (i.e., $D_2 > D_1$), however, only the lower branch of the curve could be obtained (except in one experiment with Shaft 4), and some ambiguity arose about the position of the whirling point. With the apparatus used, it was impossible to pass through the whirling points, and to get round this ambiguity an extrapolation procedure was devised.

Figure 8 (top) shows a typical amplitude–speed curve for a mild steel shaft 10 × ½ in. In this case it was possible to plot both branches of the curve, and the asymptote could be easily drawn.

Figure 8 (bottom) shows the reciprocal of the amplitude plotted against speed for the same mild steel shaft, 10 × ½ in. The method of extrapolation used to get the whirling point when only the lower branch of the curve was obtainable is illustrated. This consisted of taking a point P_r on the lower branch of the curve and producing the tangent to cut the x-axis in P_r''. The extrapolated frequency was taken as the average of P_r'' and P_r', the abscissa of P_r. The extrapolated frequencies as the points P_1, P_2, P_3, etc. move down the curve towards the whirling point can be seen to tend to a value which is near to the value of the whirling speed obtained by drawing the asymptote in Figure 8 (top).

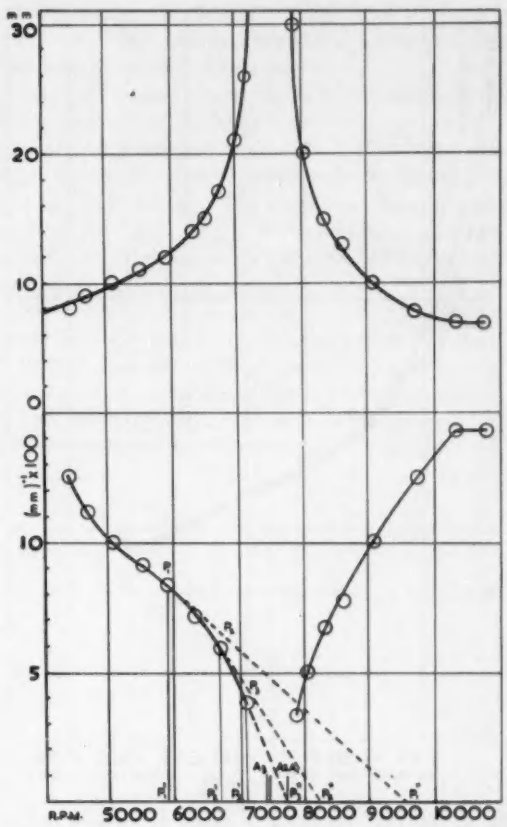

Fig. 8. Top: curve showing amplitude of whirl plotted against rotational speed; bottom: reciprocal of amplitude of whirl against rotational speed.

Tapered Shafts

The frequencies of flexural vibrations were determined as above. The critical speeds of the shafts with inverted taper were obtained by plotting both branches of the amplitude–rotational speed curve.

With shafts of normal taper, however, in only one experiment was it possible to pass through the whirling point; this was managed only once with Shaft 4. With three other tests on Shaft 4 and the remaining tests with Shafts 5 and 6, the extrapolation method had to be used. It should be pointed out here that Shaft 5 is the weakest link in the chain of observations—during the second test the shaft bent slightly. Shaft 5 was straightened since it was not convenient to get another one machined.

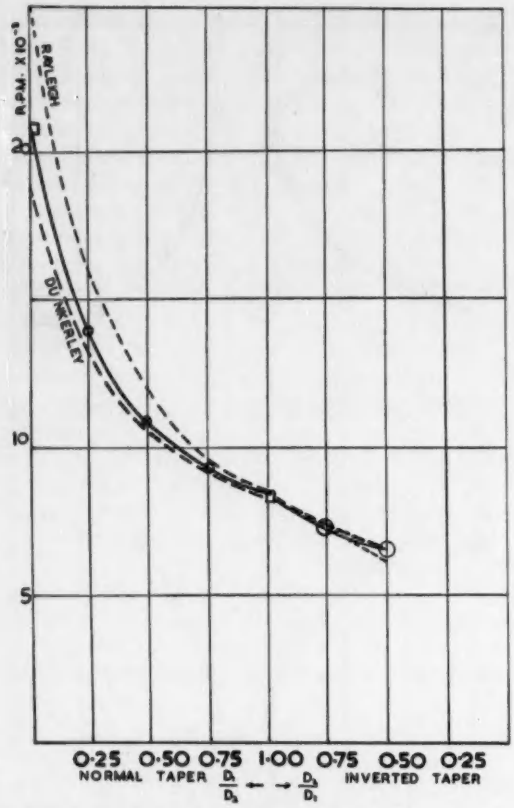

Fig. 9. Flexural vibrations of shafts in rigid mounting; □ = exact analysis, ○ = isolated in concrete.

Comparison of Results

Table VI summarizes the results obtained for the set of six mild steel shafts.

Another check point was kindly supplied by Professor R. C. Johnson. He has calculated the frequency of a truncated cone with free end diameter equal to half that of fixed end diameter by means of a Ritz method using six functions. The result was

$$\omega = 2\pi\nu = 1.156 \left(\frac{D_2}{L^2}\right)\sqrt{\frac{Eg}{\gamma}}$$

For Shaft 5 above, this formula gives a calculated frequency of 10,930 r.p.m. For this particular case the Dunkerley value is 1.7% low compared to the value with concrete and 3% low on Professor Johnson's calculated value; i.e., the extension of the Dunkerley method gives a surprisingly good result, bearing in mind its extreme simplicity.

Several tests in connection with some other work were done with cylindrical spindles of different materials. Table VII shows two typical results and is merely intended to illustrate the comparative values of vibrational frequencies and critical speeds.

In Figure 9 are plotted the experimental values of the frequencies of the set of tapered shafts when embedded in concrete. For the cylinder, the values of experiment and theory agree. Further, if the result of exact analysis for the sharp-pointed shaft is also plotted, a smooth curve can be drawn through the whole set of points. In other words, a

TABLE VI

Shaft	Theoretical frequency, calculated, r.p.m.			Experimental values of frequency of flexural vibration, r.p.m.			Rotation, critical speed by experiment, r.p.m.
	Rayleigh method	Dunkerley method	Exact analysis	Concrete	Lathe-chuck	A.C. bearings	
1	6,580	6,110	—	6,550	6,450	5,800	5,050
2	7,380	7,270	—	7,200	7,100	6,700	6,300
3	8,460	8,260	8,380	8,400	8,100	7,700	7,550
4	9,620	9,160	—	9,300	8,800	8,800	8,550
5	11,810	10,570	—	10,750	10,450	9,550	9,300
6	15,980	12,950	—	13,900	13,200	13,300	12,850

TABLE VII

Shaft	Theoretical frequency by exact analysis, r.p.m.	Frequency in lathe-chuck, r.p.m.	Frequency in A.C. bearings, r.p.m.	Rotational critical speed, r.p.m.
Brass 5/8 × 10 in	7,150	6,500	6,450	6,150
Aluminium 1/2 × 7.4 in	15,600	13,650	13,300	13,150

basic curve has been obtained for the frequency of a set of shafts of different shapes when held in a perfectly rigid mounting, this basic curve agreeing with the two well-known results of exact analysis mentioned above. Any variation in frequency due to the use of other mountings can be referred to this basic curve. Figure 9 also depicts the corresponding curves obtained by using the Rayleigh and Dunkerley methods. Comparing the Rayleigh and Dunkerley curves, it will be seen that the Dunkerley one is the better of the two both as regards overall accuracy and simplicity of formula.

In Figure 10 the results for concrete are plotted against $\sigma_D/\sqrt{5}$; if Dunkerley's formula held exactly, a straight line would be obtained. The progressive departure of the points from the Dunkerley straight line as the speed increases can easily be seen.

In Figure 11 the critical rotational speeds and the frequencies of flexural vibration in lathe-chuck and in angular contact bearings are compared with the basic curve. It should be noted that the lathe-chuck had to be tightened by hand and the degree of tightening may vary slightly from shaft to shaft. As the shafts get more and more sharp-pointed, however, the curves come together.

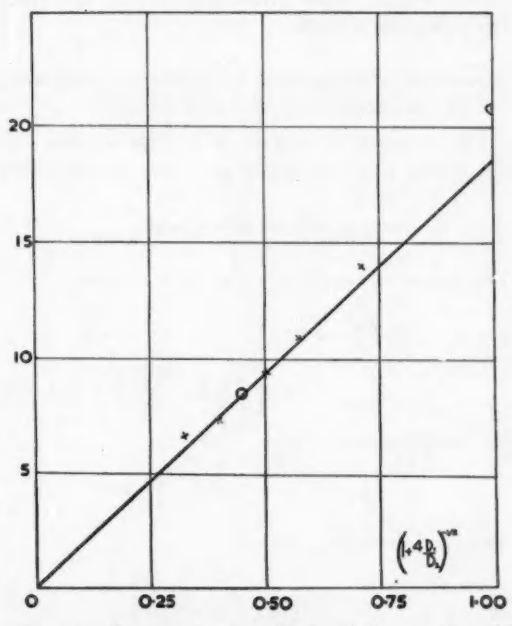

Fig. 10. Comparison of results for rigid mounting with Dunkerley's formula; ○ = exact analysis, × = in concrete, — = Dunkerley's formula.

In practice, the resonance point of a shaft is lower than the simple theoretical value and the divergence consists of two parts.

(a) The frequency of flexural vibration drops when the shaft is placed in bearings instead of being perfectly rigidly mounted. In other words, if ν_{R_0} = frequency of shaft in perfectly rigid mounting and ν_{B_0} = frequency of shaft mounted in bearings and not rotating, then it is found that $\nu_{B_0} = \chi\nu_{R_0}$ where χ ($\leqslant 1$) depends on the type of bearing used and on the amount of taper.

(b) With rotation, whirling occurs at an angular speed less than the natural frequency of the shaft. If Ω_c denotes the critical speed, then $\Omega_c = \kappa\nu_{B_0}$, where κ ($\leqslant 1$) depends on the taper of the shaft.

It is possible to obtain a theoretical expression for κ by considering the dynamics of a particular system in detail [6]. This is not true of χ, however,

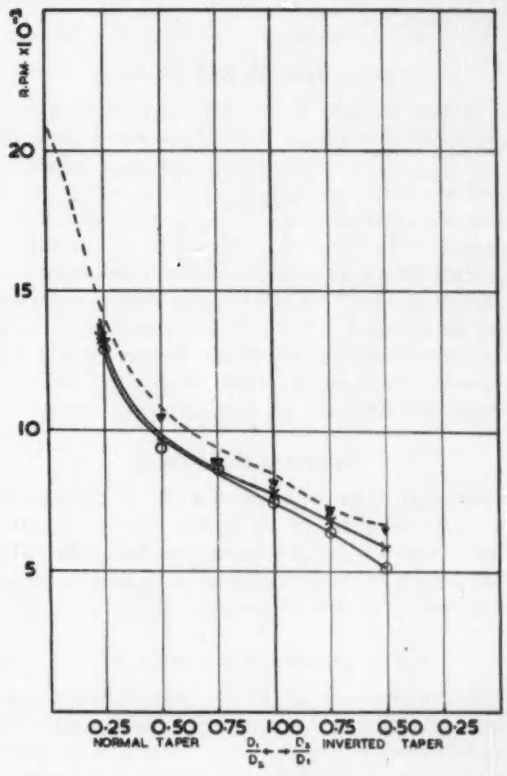

Fig. 11. Comparison of results for frequency in angular contact bearings and whirling speed with corresponding values for rigid mounting; – – – = rigid mounting, × = angular contact bearings, ○ = rotation, △ = lathe-chuck.

TABLE VIII

Shaft	Moment of inertia, lb. in.² × 100	χ	κ
1	10.65	0.88	0.87
2	3.31	0.93	0.94
3	1.72	0.92	0.96
4	1.02	0.95	0.97
5	0.67	0.89*	0.97
6	0.44	0.95	0.96

* See *Tapered Shafts*.

and it becomes necessary to rely on empirical results. As an illustration, Table VIII gives the value of χ and κ found for the particular set of shafts used in the above experiments. The corresponding values of the moments of inertia of the shafts about their axes are also given. There is some tendency for χ and κ to decrease as the moment of inertia of the shaft increases.

Textile Spindles with Packages

It was thought worthwhile to include in this paper an example of how Dunkerley's principle may be applied to calculate the natural frequency and hence the whirling speed of a vertical shaft carrying a distributed load in the form of a textile package. In Appendix III, a simple formula is derived which is easily adaptable to slide-rule calculations. The treatment is restricted to considering the effect of the distributed mass loading only. Gyroscopic effects (usually negligible) are not discussed. These effects have been dealt with by Mann and Clements [8] for cantilever shafts.

Summary of Findings

An approximate formula for the frequencies of flexural vibration of uniformly tapered circular shafts is derived by Dunkerley's method. It is also indicated how the method can be applied to actual cases met with in textile engineering.

Acknowledgments

One of the authors (D. W.) would like to acknowledge the financial support of the International Wool Secretariat for this work. Both are indebted to Professor R. C. Johnson of the Department of Mechanical Engineering of the University of Leeds for valuable discussions during the writing of this paper and to the workshop staff of the Textile Department of the University of Leeds for their cooperation.

Appendix I

The exact analysis for the problem of the vibration of a cylindrical shaft is quite straightforward and is given in almost any engineering textbook on vibrations. Timoshenko [13] gives the result of Kirchhoff's analysis of the vibration of a conical bar.

Rayleigh's method can be applied to these two cases. For the case of the vibration of a cantilever of constant cross section, the value of the fundamental frequency obtained from first approximation is 0.4% high. In the case of the sharp-pointed shaft, a simple trial function,

$$X = a_0\left(1 - \frac{x}{L}\right)^2 \tag{I.1}$$

satisfies the requisite boundary conditions (stated in the next section). Equating the maximum kinetic and potential energies gives for the circular frequency

$$\omega = 2\pi\nu = 2.291\left(\frac{D_2}{L^2}\right)\sqrt{\frac{Eg}{\gamma}} \tag{I.2}$$

which is 5% higher than is given by the exact analysis of Kirchhoff.

Deriving the Fundamental Frequencies for Uniformly Tapered Shafts by the Rayleigh Method

The moment of inertia of a cross section perpendicular to the x-axis at any point is given by

$$I_x = \frac{\pi}{64}\left[D_1 + (D_2 - D_1)\frac{x}{L}\right]^4 \tag{I.3}$$

The boundary conditions are, for a free end,

$$x = 0, \quad EI_x\frac{d^2X}{x^2} = 0,$$

$$\text{and } \frac{d}{dx}\left(EI_x\frac{d^2X}{dx^2}\right) = 0 \tag{I.4}$$

For a built-in end,

$$x = L, \quad X = 0, \quad \text{and} \quad \frac{dX}{dx} = 0$$

As a trial function, take

$$X = a_0\left[3 - 4\frac{x}{L} + \frac{x^4}{L^4}\right] \tag{I.5}$$

and this can be seen to satisfy the required boundary conditions.

Rayleigh's method [13] consists in equating the maximum potential to the maximum kinetic energy.

The maximum potential energy is given by

$$V_m = \tfrac{1}{2}\int_0^L EI_x\left(\frac{d^2X}{dx^2}\right)^2 dx \qquad (I.6)$$

By use of the above form for X, this becomes

$$V_m = \frac{E}{2}\cdot\frac{a_0^2}{L^3}\left(\frac{\pi}{64}\right)[28.80\,D_1^4 + 96.00\,D_1^3 \times (D_2 - D_1) + 123.43\,D_1^2\,(D_2 - D_1)^2 + 72.00\,D_1\,(D_2 - D_1)^3 + 16.00\,(D_2 - D_1)^4] \qquad (I.7)$$

The maximum kinetic energy is given by

$$T_m = \frac{\omega^2}{2g}\int_0^L \gamma A_x X^2 dx \qquad (I.8)$$

where A_x is the area of cross section at any point and is given by

$$A_x = \frac{\pi}{4}\left[D_1 + (D_2 - D_1)\frac{x}{L}\right]^2 \qquad (I.9)$$

By use of the above trial function the kinetic energy becomes

$$T_m = \frac{\gamma\omega^2}{2g}\cdot a_0^2 L\left(\frac{\pi}{4}\right)[2.3111\,D_1^2 + 0.9143\,D_1 \times (D_2 - D_1) + 0.1481\,(D_2 - D_1)^2] \qquad (I.10)$$

Equating the expressions for V_m and T_m gives

$$\omega = 2\pi\nu = \sigma_R\left(\frac{D_2}{L^2}\right)\sqrt{\frac{Eg}{\gamma}} \qquad (I.11)$$

where $\sigma_R = \sigma_R\,(D_1/D_2)$ and is written out explicitly in Equation 2.

Appendix II. Deriving the Fundamental Frequencies for Uniformly Tapered Shafts by Dunkerley's Method

Owing to the nature of Dunkerley's method, it is better to take axes as shown in Figure A3 with the origin at the built-in end of the shaft.

Static Case of Light Shaft with Force F Applied at Free End

As a preliminary step, it is necessary to estimate the deflection at the tip of a uniformly tapered circular shaft due to a force F acting there. Consider the bending moment at a typical cross section distance x from the fixed end; then

$$EI_x\frac{d^2y}{dx^2} = F\,(L - x) \qquad (II.1)$$

and the moment of inertia of a cross section perpendicular to the x-axis is given by

$$I_x = \frac{\pi}{64}\left[D_2 - (D_2 - D_1)\frac{x}{L}\right]^4 \qquad (II.2)$$

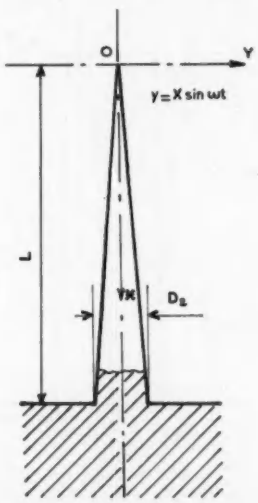

Fig. A1. Sharp-pointed shaft built in at its base.

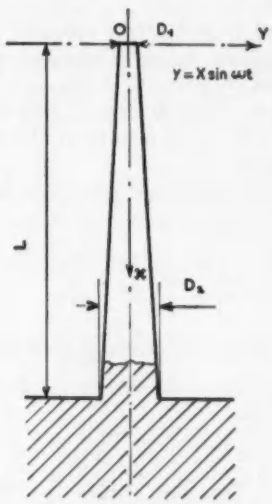

Fig. A2. Uniformly tapered shaft built in at one end.

Provided $I_x \neq 0$, the differential equation for the deflection at any point along the shaft can be written in the form

$$\frac{d^2y}{dx^2} = \left(\frac{64F}{\pi E}\right) \frac{L - x}{\left[D_2 - (D_2 - D_1)\frac{x}{L}\right]^4} \quad \text{(II.3)}$$

By use of the boundary conditions, this can be integrated and Δ, the deflection at the tip, obtained by putting $x = L$ in the expression for y. Hence, for $D_1 \neq D_2$

$$\Delta = \frac{1}{3}\left(\frac{FL^3}{EI_2}\right)\left(\frac{D_2}{D_1}\right) \quad \text{(II.5)}$$

where I_2 refers to the fixed end of the shaft; i.e.

$$I_2 = \frac{\pi}{64} D_2^4 \quad \text{(II.6)}$$

For the case $D_1 = D_2$, the differential equation becomes

$$\frac{d^2y}{dx^2} = \left(\frac{64F}{\pi E}\right)\left(\frac{1}{D_2^4}\right) \quad (L - x) \quad \text{(II.7)}$$

Integrating twice, using the boundary conditions, and putting $x = L$, one obtains

$$\Delta = \frac{1}{3}\left(\frac{64F}{\pi E}\right)\left(\frac{L^3}{D_2^4}\right) \quad \text{(II.8)}$$

The same result can be obtained by putting $D_1 = D_2$ in Equation II.5.

For the case $D_1 = 0$, the expression for the deflection diverges as the tip is approached.

For the case $D_2 = 0$, the expression for the deflection becomes infinitely large. Physically, since the fixed end is now only a pinhead, the whole shaft merely topples over.

A general expression for the force per unit deflection follows immediately from Equation II.5:

$$\mu = \frac{F}{\Delta} = \frac{3EI_2}{L^3}\left(\frac{D_1}{D_2}\right) \quad \text{(II.9)}$$

Flexural Vibrations of Uniformly Tapered Shafts

The area of a cross section perpendicular to the x-axis is given by

$$A_x = \frac{\pi}{4} D_x^2 = \frac{\pi}{4}\left[D_2 - (D_2 - D_1)\frac{x}{L}\right]^2 \quad \text{(II.10)}$$

Consider the element of the shaft shown in Figure 4 of weight $\gamma A_x \delta x$ and suppose that the rest of the shaft is weightless. Let τ_x be the period of vibration of this element of weight at the end of a light uniformly-tapered shaft of length x. Then, apply the well-known formula for the period of vibration of a light shaft with a mass at its tip,

$$\left(\frac{\tau_x}{2\pi}\right)^2 = \frac{\gamma A_x \delta x}{g\mu_x} \quad \text{(II.11)}$$

where μ_x is the force per unit deflection at point x and is given by

$$\mu_x = \frac{3EI_2}{x^3} \cdot \left(\frac{D_x}{D_2}\right) \quad \text{(II.12)}$$

from Equation II.11 above.

Dunkerley's principle [4] gives τ, the period of vibration of the shaft, as

$$\left(\frac{\tau}{2\pi}\right)^2 = \Sigma\left(\frac{\tau_x}{2\pi}\right)^2 = \Sigma \frac{\gamma A_x \delta x}{g\mu_x} = \Sigma \frac{\pi}{4}\left(\frac{\gamma}{Eg}\right)\left(\frac{D_2}{3I_2}\right) D_x x^3 \delta x \quad \text{(II.13)}$$

so that

$$\left(\frac{\tau}{2\pi}\right)^2 = \frac{\pi}{4}\left(\frac{\gamma}{Eg}\right)\left(\frac{D_2}{3I_2}\right) \times \int_0^L \left[D_2 - (D_2 - D_1)\frac{x}{L}\right] x^3 \, dx \quad \text{(II.14)}$$

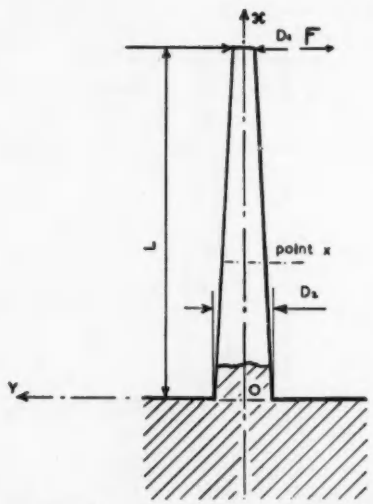

Fig. A3. Static force F applied at free end of a uniformly tapered light shaft.

taking the limit $\delta x \to 0$. Therefore, we see that

$$\left(\frac{\tau}{2\pi}\right)^2 = \left(\frac{4L^4}{3D_2^2}\right)\left(\frac{\gamma}{Eg}\right)\cdot\frac{1}{5}\left(1 + \frac{4D_1}{D_2}\right)$$

and since $\omega = 2\pi/\tau$, it follows that

$$\omega = 2\pi\nu = \sigma_D\cdot(0.8661)\left(\frac{D_2}{L^2}\right)\sqrt{\frac{Eg}{\gamma}} \quad \text{(II.15)}$$

where σ_D is a shape factor with a simple form given by

$$\sigma_D{}^2 = \frac{5}{1 + 4\left(\frac{D_1}{D_2}\right)} \quad \text{(II.16)}$$

Appendix III. Application of Dunkerley's Principle to Estimate the Effect of the Mass of a Package on the Whirling Speed of a Spindle

In everyday machinery, the bearings will be worn to a certain extent, but the effect of bearing clearance on whirling speeds is assumed to be negligible for clearances up to 0.002–0.003 in. Tests by Downham [3] on the whirling of shafts provide reasonable justification for this.

Several different shapes could be assumed for the package. In most cases, however, the resulting formulas are cumbersome to use. The example illustrated in Figure A5 is of special interest since the formulas derived by mathematical analysis lend themselves to considerable simplification for textile engineering purposes.

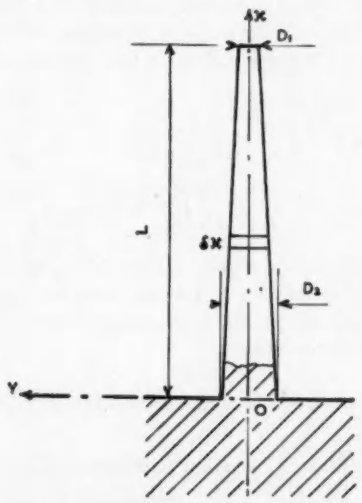

Fig. A4. Uniformly tapered shaft built in at one end.

The spindle blade only is anchored at its base, the package being merely carried by the shaft. Further, suppose that the yarn is wound on the bobbin to give a package of parabolic profile.

The cross section in a vertical plane of the yarn package (refer to Figure A5) is parabolic; by taking axes as shown, the equation for the parabola may be expressed in the form

$$Y = a + bx - cx^2 \quad \text{(III.1)}$$

When $2Y = D_t$, x is given by

$$cx^2 - bx + (\tfrac{1}{2}D_t - a) = 0$$

and from Figure A5, it can be seen that the roots are λ and L; i.e.,

$$\lambda + L = b/c$$

$$L = \frac{(\tfrac{1}{2}D_t - a)}{c} \quad \text{(III.2)}$$

The profile of the package is symmetrical about the line $x = \lambda + L/2$, since dY/dx vanishes for this value of x. If $(\frac{1}{2}D_t + D^*)$ is the corresponding maximum value of Y,

$$\tfrac{1}{2}D_t + D^* = a + b\left(\frac{\lambda + L}{2}\right) - c\left(\frac{\lambda + L}{2}\right)^2 \quad \text{(III.3)}$$

Substitution of b and c from Equation III.2 gives

$$a = \tfrac{1}{2}D_t - \frac{4\lambda L}{(\lambda - L)^2}D^* \quad \text{(III.4)}$$

and the use of Equation III.2 again also gives

$$b = \frac{4(\lambda + L)}{(\lambda - L)^2}D^*$$

$$c = \frac{4}{(\lambda - L)^2}D^* \quad \text{(III.5)}$$

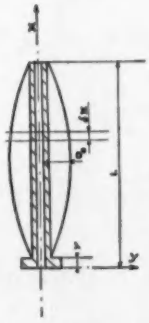

Fig. A5. Textile package with parabolic profile.

Consider an elementary slice of the package taken perpendicular to the x-axis; the weight of the slice (wt.) is given by

$$\text{wt.} = \frac{\pi}{4}[\gamma_s D_s^2 + \gamma_t (D_t^2 - D_s^2) + \gamma_y (4Y^2 - D_t^2)]\,\delta x$$

for $\lambda \leqslant x \leqslant L$, and by

$$\text{wt.} = \frac{\pi}{4}\gamma_t (D_b^2 - D_s^2)\,\delta x \qquad \text{(III.6)}$$

for $0 \leqslant x \leqslant \lambda$. The period of vibration of this mass at the end of a light cantilever of diameter D_s and length x is given by

$$\tau_x^2 = \frac{1}{g}(\text{wt.})\cdot\frac{x^3}{3EI} \qquad \text{(III.7)}$$

assuming that the stiffness E of the blade is unaffected by the addition of a package. The calculation can be carried out for a tapered shaft, but for simplicity it is assumed here that the blade is uniform, with I as the moment of inertia of the area of cross section. It should be noted that starting from a ghost shaft of the same shape and size as the steel blade, the actual system is built up by the addition of a series of elementary masses (see also Appendix II). The spindle blade is the only component of the system that is firmly anchored at one end; consequently the ghost shaft is chosen to be of the same size and shape as this blade.

The extension of Dunkerley's principle is now applied to obtain the period of vibration τ for the complete system.

$$\tau^2 = \lim_{\delta x \to 0} \sum_0^L \tau_x^2 \qquad \text{(III.8)}$$

Use of Equations III.6 and III.7 in Equation III.8 gives

$$\tau^2 = \frac{\pi}{12EIg}\Big[\gamma_s \int_0^L D_s^2 x^3\,dx + \gamma_t \int_0^\lambda (D_b^2 - D_s^2)x^3\,dx + \gamma_t \int_\lambda^L (D_t^2 - D_s^2)x^3\,dx + \gamma_y \int_\lambda^L [4(a + bx - cx^2)^2 - D_t^2]x^3\,dx\Big] \qquad \text{(III.9)}$$

If τ_0 is the period of vibration of the spindle blade itself, it can be shown by substitution that

$$\tau_0^2 = \left(\frac{\pi}{12EIg}\right)\gamma_s L^4 \left(\frac{D_s}{4}\right)^2 \qquad \text{(III.10)}$$

$$= \frac{4}{3}\left(\frac{L^4}{D_s^2}\right)\left(\frac{\gamma_s}{Eg}\right)$$

since $I = \pi\pi/64\ D^4$. By substitution of a, b, and c, Equation III.9 can be reduced to

$$\left(\frac{\tau}{\tau_0}\right)^2 = 1 + \left(\frac{\gamma_t}{\gamma_s}\right)\left(\frac{D_t^2}{D_s^2} - 1\right) + \xi_1\left(\frac{\lambda}{L}\right)\cdot\left(\frac{\gamma_t}{\gamma_s}\right)\left(\frac{D_b^2 - D_t^2}{D_s^2}\right) + \frac{32}{15}\left(\frac{\gamma_y}{\gamma_s}\right)\left(\frac{D^*}{D_s}\right)\left(\frac{D_t}{D_s}\right) \times \left[\xi_2\left(\frac{\lambda}{L}\right) + \frac{5}{7}\left(\frac{D^*}{D_t}\right)\cdot\xi_3\left(\frac{\lambda}{L}\right)\right] \qquad \text{(III.11)}$$

where

$$\xi_1\left(\frac{\lambda}{L}\right) = \left(\frac{\lambda}{L}\right)^4$$

$$\xi_2\left(\frac{\lambda}{L}\right) = 1 + \frac{1}{2}\left(\frac{\lambda}{L}\right) - \frac{1}{2}\left(\frac{\lambda}{L}\right)^3 - \left(\frac{\lambda}{L}\right)^4$$

$$\xi_3\left(\frac{\lambda}{L}\right) = 1 + \frac{4}{5}\left(\frac{\lambda}{L}\right) - \frac{4}{5}\left(\frac{\lambda}{L}\right)^3 - \left(\frac{\lambda}{L}\right)^4 \qquad \text{(III.12)}$$

These three function of (λ/L) are shown graphically in Figure A6 for the complete range $0 \leqslant \lambda/L \leqslant 1$.

If, as with ordinary textile packages, the terms in (λ/L) can safely be neglected, the formula simplifies to

$$\left(\frac{\tau}{\tau_0}\right)^2 = 1 + \left(\frac{\gamma_t}{\gamma_s}\right)\left(\frac{D_t^2}{D_s^2} - 1\right) + \frac{32}{15}\left(\frac{\gamma_y}{\gamma_s}\right)\left(\frac{D^*}{D_s}\right)\left(\frac{D_t}{D_s}\right)\left[1 + \frac{5}{7}\left(\frac{D^*}{D_t}\right)\right] \qquad \text{(III.13)}$$

The justification for this may be seen from a simple numerical example. Consider a woolen mule type of package where $D_t = D_b$, reasonable values for the other factors being

$$\frac{\gamma_t}{\gamma_s} = \frac{1}{8}\ \text{(paper:steel)}$$

$$\frac{\gamma_y}{\gamma_s} = \frac{1}{20}\ \text{(woolen package:steel)}$$

$$\frac{D_t}{D_s} = \frac{13}{11}\ \text{(for example)}$$

Then the exact formula gives the equation below.

$$\left(\frac{\tau}{\tau_0}\right)^2 = 1.0496 + 0.0315 \cdot \xi_2 \left(\frac{\lambda}{L}\right) \cdot \left(\frac{D^*}{D_s}\right) + 0.0191 \cdot \xi_3 \left(\frac{\lambda}{L}\right) \cdot \left(\frac{D^*}{D_s}\right)^2 \quad \text{(III.14)}$$

Figure A7 shows (ν/ν_0) plotted agains (D^*/D_0) for two values of (λ/L). By referring to the ξ_2 and ξ_3 curves of Figure A6, two (λ/L) values were taken: at the beginning of the curve $(\lambda/L) = 0$ and at approximately the peak values $(\lambda/L) = 0.45$. For all practical purposes, the two curves shown in Figure A7 are the same. Further, with all textile packages, no points beyond the maxima of the ξ_2 and ξ_3 curves need be considered, since in textile practice the values of λ are never sufficiently large for this to be necessary. Consequently, it is justifiable to neglect all terms in (λ/L) and use Equation III.14.

Some Observations on a Mule Spindle

Some observations were made on a commercial spindle of the Rabbeth type (a name given to a particular type of roller bearing spindle suitable for use on high speed mule spinning frames).

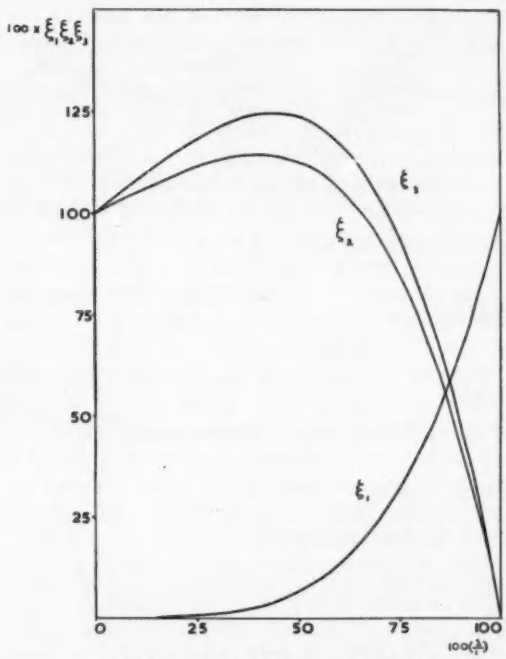

Fig. A6. The functions ξ_1 ξ_2, and ξ_3.

In this case, the spindle is not mounted in rigid bearings. From Figure A8 it will be seen that the roller bearings are allowed flexibility by the application of a flexible insert. It can be shown by mechanical analogy that the effect upon the spindle blade is the introduction of a second critical speed. These two critical speeds are usually near to the separate critical speeds of the blade and bearing insert respectively.

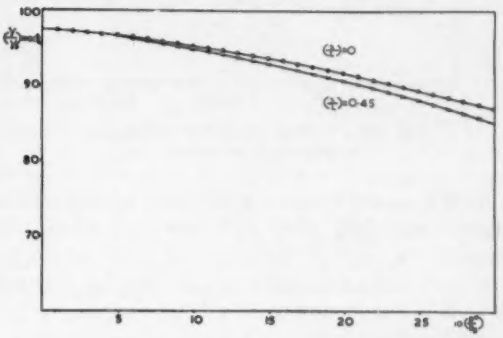

Fig. A7. Typical reduction in whirling speed due to addition of package.

Fig. A8. Rabbeth spindle. ("The Asa Lees Woollen Mule," Platt Bros. (Sales) Ltd.)

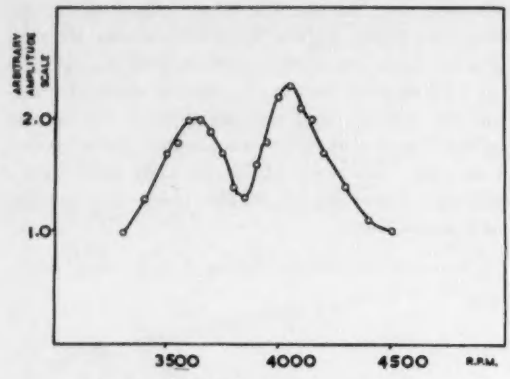

Fig. A9. Typical amplitude–speed curve showing two peaks.

In Figure A9 a typical amplitude–speed curve is shown illustrating these two resonance points. It should be noted that the amplitude scale is quite an arbitrary one. In general, one can say that for each flexibility introduced there will be a corresponding critical speed.

The following Table I shows how the two critical speeds are affected by winding yarn onto the paper tube to give a complete package or cop. As more and more yarn is wound on, the first peak diminishes in intensity until, for a fully wound package, only one peak is observed. A full analysis of this system has not yet been attempted.

TABLE I. Whirling Speeds, r.p.m.*

	Insert	Blade
Blade	3550	3970
Blade and tube	3430	4020
Blade and tube one quarter full of yarn	3500	3950
Blade and tube half full of yarn	3230	3530
Blade and tube with fully wound package	2550	2550

* The accuracy of estimating the position of the peaks is of the order of ±25 r.p.m.

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Correction

The listings under "Letters to the Editor" in the March 1959 table of contents should read as follows.

A Useful Stain for Inclusion and Surface Damage Detection in Viscose Rayon Filaments. *E. Corwith Jolliff* 279
A Note on the Degradation of Jute Cellulose on Storage. *H. Chatterjee and A. K. Mazumdar* 282
The Hydrogen → Deuterium Exchange Reaction in Stretched Keratin. *E. G. Bendit, M. Feughelman, R. D. B. Fraser, and T. P. MacRae* 284
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Physical Properties of Mercerized and Decrystallized Cottons

Part I: Effects of Swelling Solutions on Fibers and Yarns

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Abstract

Yarns from samples of Pima S-1, Hopi Acala, and Coker 100 Wilt varieties were scoured, chloroform extracted, mercerized, and decrystallized with anhydrous ethylamine without tension. Breaking loads for yarns immersed in solutions when compared to those in water were essentially unchanged by ethylamine but decreased appreciably by sodium hydroxide. Untreated yarns in water showed decreases in strength with increases in water temperature. Sodium hydroxide caused yarn to shrink in length as much as 35% but ethylamine only about 17%. Yarn shrinkages were related to increases in cross-sectional areas of fibers and to cell sizes of the two complexes. Fiber lengths after treatments were unchanged by scouring or extraction but decreased by the sodium hydroxide and the ethylamine. Mercerization at normal length caused a reduction in the percentage decrease in single fiber and bundle tenacities as the gauge length was increased. Strength increases during mercerization are attributed to increased uniformity of strength along the fiber length.

Introduction

While mercerization is one of the oldest and most successful chemical treatments of cotton and has had extensive and continuous study, there still remains some uncertainty about its effect on certain physical properties of cotton fibers and yarns. The general belief is that the change in tensile properties is associated with the reduced crystallinity, as indicated by reaction rate studies [6, 20, 24]. However, the relatively new method of reducing crystallinity by treatment with ethylamine [16, 28, 29] causes changes in tensile properties differing from those of mercerization [18, 19]. While decrystallization has been advanced primarily as a pretreatment to increase reactivity for subsequent chemical treatments, especially cross-linking treatments not involving aqueous solutions [16], it is also important to determine the difference in effect of these two swelling treatments on other physical properties of fibers and yarns.

Of special interest is the effect of tension during these treatments where considerable swelling occurs in the fibers. Mercerization is usually carried out with sufficient tension on the textile product to provide yarns or fabrics with dimensions equivalent to those of the untreated. The reason often given for the tension is to prevent a loss in yardage. However, the high luster produced by mercerization with tension is still one of the main purposes of the treatment [4, 8]. It is generally known that tension during treatment has a large effect on the tensile properties of cotton fibers and yarns [2, 8, 15, 17]. An advantage has recently been taken of the special properties imparted by mercerization without tension in making conformative gauze for bandages [9]. Recent investigations have shown that the variety or growth conditions affect the extent of change in physical properties of the fibers as a result of mercerization [18, 21].

In the present study, two samples of cotton representing extremes in response to mercerization and one of average characteristics were mercerized and decrystallized with ethylamine under several conditions of strain. The properties discussed in Part I include stress–strain properties of yarns in swelling solutions, swelling characteristics of the solutions, and changes in the length, tenacity, and elongation of the fibers during treatment.

[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, United States Department of Agriculture.

Experimental

Samples

The three samples selected were Pima S-1, a strong, high elongation American-Egyptian type cotton; Hopi Acala 50, which has high fiber strength at short gauge lengths but loses considerable strength as gauge length is increased; and Coker 100 Wilt, an average American upland variety from commercial production. Yarns of tex 36.9 ×2 (cotton 16/2) construction, 12 turns/in. singles and 11.4 turns/in. in ply were spun for each of the three samples. All Pima S-1 samples were from combed stock.

Treatments

Yarns were mercerized at 25° C. in 20% NaOH solution containing Dypenol S-E wetting agent. The skeins were thoroughly washed with tap water, given a 0.5% acetic acid sour, and a final thorough wash in tap water. Yarn skeins were mercerized without tension (i.e., slack mercerized) and while held at normal length using an apparatus previously described [10].

Decrystallization was carried out as described by Segal et al. [16, 28]. The samples were soaked 4 hr. in anhydrous ethylamine at a temperature between 0° and 10° C. After the soaking, the ethylamine was drained off and the samples immediately extracted with chloroform in a Soxhlet extractor. A small amount of phosphoric acid in the boiling flask converted extracted ethylamine to a nonvolatile salt. Several skeins of the mercerized and decrystallized yarns were boiled in water for 1 hr. to partially restore their crystallinity [28].

Control samples, consisting of untreated yarn in skeins, were scoured by heating for 6 hr. in 1.5% NaOH at 15 lb./sq. in. and skeins extracted 6 hr. in a Soxhlet extractor with chloroform. Also, a series of combed bundles of fibers was prepared, then treated while held loosely between stainless steel screens. Such combed bundles of the three varieties were chloroform extracted, slack decrystallized, and slack mercerized.

Testing

Single fiber and bundle tests were made on fibers taken from treated yarns and bundles. Single fiber tests were made with the TRI-Schaevitz tester.[2] The fibers to be tested were taken from the modal length group obtained by sorting the fibers for length analysis with the Suter-Webb sorter. The fibers were mounted and tested for breaking load and elongation as previously described [18]. The center weight fineness (linear density) was determined by weighing and counting a bundle of 500 or more fibers cut to 1.17-cm. length. Tenacity was calculated from the average breaking load for at least 100 fibers and average center weight fineness.

Bundle tenacities and elongations were determined with the Stelometer[2] [14, 22], using bundles prepared by combing small tufts from both directions [1a]. The combed bundles were allowed to recondition overnight and placed in the jaws for testing according to the Stelometer method [1b].

The stress–strain curve of yarns while immersed in various swelling media was obtained with the apparatus shown in Figure 1. The test chamber A was constructed of glass with fittings at the bottom for controlling movement of liquids and at the top for reducing pressure to insure good penetration by the liquids. To control temperature, the chamber was wrapped with tubing through which coolant was pumped. The yarn was doubled and clamped at a 10-in. gauge length between clamp B and the bottom hook C. The yarn was elongated at a constant rate by a motorized screw D. Load was recorded with a variable linear-differential transformer inserted in a proving ring E, the electrical output recorded with a modified Brown recorder [26].

[2] Use of a company and/or product named by the Department does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

Results and Discussion

Stress–Strain Properties of Yarns and Fibers in Swelling Solution

In Figure 2 are given typical stress–strain curves of Hopi Acala yarns after being swollen slack with 19% sodium hydroxide solution, Curve A, and at normal length, Curve B; swollen in ethylamine at corresponding strains, respectively, Curves C and D; and held at normal length when swollen with water at 10° and 50° C., Curves E and F. The rate of extension, 24%/min., is comparable to the rate in other yarn test methods. Although strength of cotton yarn is generally increased by wetting at normal temperatures, Curves E and F show that wet strength of untreated yarns decreases with increasing temperature. At a temperature about 50° C., the yarns appear to pull apart instead of breaking, Curve F, suggesting that such temperatures reduce interfiber

friction, which is important in yarn strength. The scoured and extracted yarns did not pull apart at temperatures below 64° C., although slight losses of strength with increasing temperature were observed. Observations indicated that nonswelling liquids such as mineral oil and xylene also increased yarn strength above that at standard atmospheric conditions.

Yarns swollen slack contracted in length up to 35% when swollen in NaOH, Curve A, as compared to about 17% in ethylamine, Curve C. The breaking loads for yarns of Hopi Acala and Pima S-1 when averaged showed a 34% strength loss in the NaOH and a slight decrease in ethylamine as compared to their wet strengths, Figure 2. The extension of these yarns beyond their normal length when strained to break was less in NaOH and ethylamine than in water. Yarns held at normal length when swollen in NaOH were stronger and extension beyond normal length was greater than for those treated slack. The extension of a yarn in a liquid sets an upper limit to the strain which can be imposed on a skein during treatment.

Yarns strained dry to above 10% of the elongation at break showed a drop in stress when swollen in the NaOH solution, while those strained less than 10% of the elongation at break increased the stress when swollen in the solution. A strain at which no stress change occurs upon swelling in NaOH, noted also for single fibers, suggests an equilibrium condition in which the swelling pressure of the solution between the cellulose chains, fibrils, etc. is balanced by components of the tension in the cellulose chains. A strain value of equilibrium tension during treatment exists also for yarns treated with ethylamine. At strains above this equilibrium tension, the loss in tension during swelling is much less for ethylamine than for the mercerization.

The lengths of fibers from samples are given in Table I. The changes in fiber length are consistent with those previously reported [18]. Slack mercerization results in a larger contraction in length than slack decrystallization. Microscopical observations of the changes in length and diameter of untreated fibers indicate that they are not swollen to greater volume in ethylamine than in mercerizing strength caustic, Table II. As the crystalline complex unit cell is larger in ethylamine than in sodium hydroxide [7, 27], the larger cross-sectional swelling of the fibers in sodium hydroxide must result from a larger swelling in the noncrystalline areas. Such differential swelling between crystalline and amorphous cellulose may have a large influence upon the contraction in length of fibers upon swelling, since the cellulose chains, each of which passes through several crystalline and amorphous regions, must then take a zig-zag course when swollen with NaOH. This would explain also the large nonrecoverable elongation of slack mercerized fibers. Except for the influence of the spiral structure of the fibers, uniform swelling between the crystalline and amorphous areas should produce little contraction in length of highly oriented fibers.

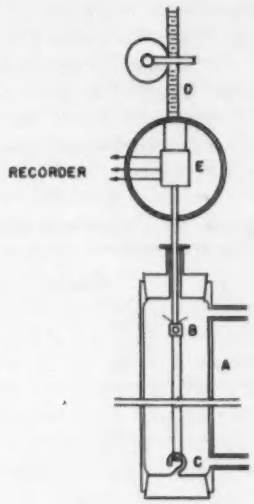

Fig. 1. Apparatus for measuring load–elongation properties of yarns while in solutions.

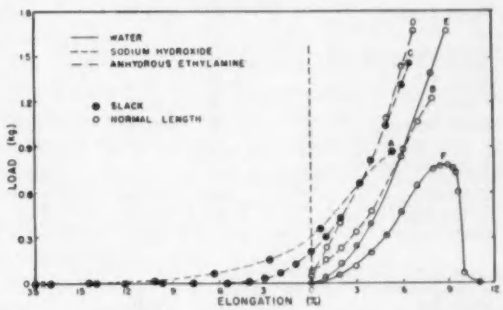

Fig. 2. Load–elongation curves for yarns of Hopi Acala cotton while in swelling solutions. Curves A and B for yarns swollen in sodium hydroxide at 25° C. while slack and at normal length, respectively; Curves C and D swollen with ethylamine at corresponding strains; and Curves E and F for yarns at normal length and swollen with water at 10° C. and 50° C., respectively.

Effect of Gauge Length

The linear density and tensile properties of single fibers at two gauge lengths for fibers taken from yarns of the Pima S-1 and Hopi Acala samples are given in Table III.

The single fiber tenacities are plotted as a function of gauge length in Figure 3, according to the relation derived by Peirce [23] from considerations of the uniformity of strength along the fiber length. Also, in Figure 3 are plotted the corresponding bundle tenacities at gauge lengths calculated as described in an earlier investigation [22].

The large dependence in cotton of single fiber tenacity on gauge length was shown by Grant and Morlier [11]. A similar dependence of bundle tenacity on gauge length has been observed by others [25, 32]. Figure 3 shows that the bundle tenacities as well as the single fiber tenacities can be used to study the strength–length uniformity and the variation in this factor among varieties and treatments.

A convenient measure of the uniformity of strength along the fiber length is the percentage drop in tenacity between two gauge lengths, Table IV. The differences in decreases of tenacity with increases of gauge lengths for flat bundles reported by Brown [3] and Hertel [13] indicate differences in strength–

TABLE I. Length of Cotton Fibers from Mercerized and from Decrystallized Yarns

Treatment and sample	Length		C.V., %
	Upper quartile, in.	Mean, in.	
Untreated			
Pima S-1	1.43	1.24	22
Coker 100	1.15	0.92	32
Hopi Acala	1.20	0.98	32
Scoured			
Pima S-1	1.40	1.21	22
Coker 100	1.15	0.91	30
Hopi Acala	1.19	0.98	34
Chloroform extracted			
Pima S-1	1.40	1.22	22
Coker 100	1.18	0.94	34
Hopi Acala	1.20	0.98	32
Ethylamine treated slack			
Pima S-1	1.33	1.16	23
Coker 100	1.10	0.88	34
Hopi Acala	1.13	0.91	32
Mercerized slack			
Pima S-1	1.20	1.05	22
Coker 100	1.00	0.80	33
Hopi Acala	1.09	0.87	33
Mercerized normal length			
Pima S-1	1.40	1.21	22
Coker 100	1.15	0.90	32
Hopi Acala	1.18	0.97	32

TABLE II. Differential Swelling of Crystalline and Amorphous Regions of Cotton in 19% NaOH and Anhydrous Ethylamine (0.5 mm. Lengths of Hopi Acala Fibers)

Swelling agent	Relative to untreated			Crystalline unit volume [7]	
	Area	Length	Volume	$(A°)^3$	Rel. to untreated [7]
Untreated	1.0	1.00	1.00	660	1.00
Ethylamine	2.4	0.90	2.16	1400	2.12
19% NaOH	2.7	0.80	2.16	1120	1.70

TABLE III. Linear Density and Tensile Properties of Single Fibers from Untreated, Decrystallized, and Mercerized Yarns of Pima S-1 and Hopi Acala Cottons

Identification	Linear* density, tex	Breaking load			Elongation	
		g.	Increase, %	C.V., %	%	C.V., %
2.7-mm. gauge length						
Pima S-1						
Untreated	.143	7.13		35	11.9	30
Merc. N.L.†	.136	7.17	1	29	11.1	25
Hopi Acala						
Untreated	.178	8.20		38	7.7	32
Merc. N.L.†	.177	9.15	12	33	8.9	30
7.8-mm. gauge length						
Pima S-1						
Untreated	.143	6.01		39	9.9	27
Decry. slack	.142	6.15	2	41	12.7	27
Merc. slack	.157	6.34	5	30	19.4	19
Merc. N.L.†	.142	6.74	12	24	9.1	24
Hopi Acala						
Untreated	.178	5.04		44	6.1	31
Decry. slack	.193	5.88	17	41	8.4	32
Merc. slack	.197	6.88	37	39	13.0	29
Merc. N.L.†	.177	6.99	39	34	6.2	27

* Linear density of 1.17 cm. from center of fiber.
† Normal length.

length uniformity among cotton samples. Generally the barbadense cottons are more uniform than American upland varieties [18, 30, 31]. The percentage drop in bundle and single fiber tenacity between gauge lengths of 2.7 and 7.8 mm. is shown in Table IV for each of the samples in Figure 3. It is seen that whether single fiber or bundle tenacities are used, the Pima is always most uniform and that mercerization increases uniformity.

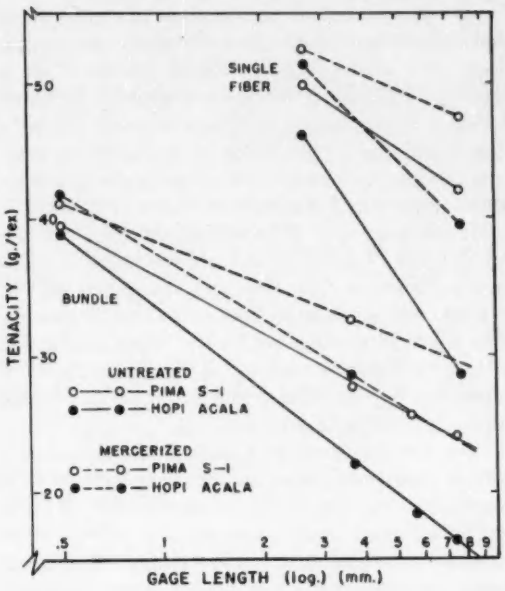

Fig. 3. The relationships of tenacity to gauge length for single fibers and fiber bundles for untreated and mercerized at normal length as bundles and yarns.

TABLE IV. Single Fiber and Bundle Tenacities at 2.7- and 7.8-mm. Gauge Lengths for Untreated and Mercerized Cottons

Sample identification	Test method	Tenacity: Gauge length 2.7 mm., g./tex	Tenacity: Gauge length 7.8 mm., g./tex	Tenacity: Decrease, %
Pima S-1				
Untreated	S. fiber	49.8	42.0	15.6
Untreated	Bundle	29.5	24.0	18.6
Merc. N.L.*	S. fiber	52.8	47.5	10.0
Merc. N.L.	Bundle	34.0	29.3	13.6
Hopi Acala				
Untreated	S. fiber	46.1	28.3	38.6
Untreated	Bundle	24.7	15.8	36.0
Merc. N.L.*	S. fiber	51.7	39.5	23.6
Merc. N.L.	Bundle	30.7	23.3	24.1

* Normal length.

The uniformity of strength along fiber length which affects the coefficient of variation of both single fiber breaking load and elongation at break, Table III, was pointed out in an earlier publication [18]. Single fiber breaking load varies mainly for three reasons: variation in average area of cross-section between fibers, variation in intrinsic strength between fibers, and variation in breaking load along the length of the fiber. The first cause above can be eliminated by measuring the linear density or the cross-sectional area of the individual fibers, from which individual fiber tenacities are calculated. Observations in another investigation indicate that the coefficient of variation is reduced from about 45% for single fiber breaking loads to about 35% for individual fiber tenacities. The second cause of variance is the differences in intrinsic strength among fibers of a sample which may result from growth conditions or chemical and physical treatments. This can be separated from the other causes, to some extent, by making individual fiber tenacity measurements at very short gauge lengths. The third cause is thought to result from variations in cross-sectional area along the fiber and to variations in intrinsic strength along the fiber as a result of strains, damaged areas, etc. Structural reversals as a preferred location of weak places along the fiber have been established; their effect on fiber strength may be changed by wetting, mercerization, and other treatments [33].

The coefficient of variation of elongation at break of single fibers, Table III, is not affected directly by cross-sectional area, but is affected by the other causes affecting variation of breaking load and is therefore generally smaller than that of breaking load [18]. The coefficients of variation of both breaking load and elongation at break were decreased by mercerization [18].

There is some uncertainty in the literature as to whether mercerization increases or decreases fiber strength [2, 5, 12]. A definite gauge length was usually used in earlier studies, and in no instance was the effect of varying gauge length studied. The data, Table III, indicate that mercerization, either slack or with tension, increases fiber breaking load

considerably at longer gauge lengths and less so at short gauge lengths. The tenacity of fibers and fiber bundles from yarns mercerized with tension was increased, even at the gauge length of zero spacer (about 0.5 mm.). However, slack mercerization in some cottons decreased bundle tenacity at zero spacer, even for the uniform Pima S-1 sample. This effect is largely the result of increased fiber linear density, since the fiber shrinks in length and swells in cross-sectional area. If tenacities were based on the linear density at the instant of break, smaller differences in the tenacities of fibers slack mercerized and mercerized at normal length would be found. The slack mercerized fibers elongate and decrease much more in cross-sectional area than those treated with tension.

Another investigation [18] has shown that characteristics of the original sample affect the extent of change of fiber strength properties on mercerization. In the present study the tenacities of Hopi Acala and Coker samples were increased more by mercerization than that of Pima S-1.

The strength changes resulting from mercerization can be explained as a relief of strains in fiber structure set up during the drying and crystallization of cellulose while fibers are in the bolls. Mercerization, by reducing the crystallinity and allowing greater swelling, could permit more freedom of movement between fiber segments, such as crystallites, microfibrils etc., thus strengthening the weak places by relief of these strains. The increases in strength at the longer are greater than those at the shorter gauge lengths because of the number of weak places included in the test section. Also, strength increases with mercerization are larger for cottons which have the greatest changes in strength with gauge length, such as the sample of Hopi Acala, than in cottons of uniform fibers, such as the Pima S-1.

Decrystallization by ethylamine has a smaller effect on most of the fiber tensile properties measured than does mercerization. Also, qualitative observations show that the luster of decrystallized bundles was not as pronounced as that of mercerized. These differences may also be associated with the differences between sodium hydroxide and ethylamine in differential swelling of the crystalline and amorphous phase, as discussed earlier.

Conclusion

Mercerization, both slack and with tension, increases the strength uniformity along fiber length as measured on both bundles and single fibers. This is attributed to an increase in strength of the weakest places along the fiber, thus resulting in greater gains in average fiber strength at the longer than the shorter gauge lengths. The greater strength uniformity is reflected in the decrease in coefficient of variation in both single fiber strengths and elongations after mercerization. These factors offer a plausible explanation for greater strength increases during mercerization of samples with lower strength–length uniformity than those of higher uniformity. Decrystallization changes only slightly the strength–length uniformity but usually increases fiber strength.

Measurements of the swelling of fibers in ethylamine and 19% NaOH indicate that the differential swelling between crystalline and amorphous regions is smaller in ethylamine than in sodium hydroxide. This offers an explanation for the larger contraction in length, higher elongation at break, and greater permanent set at high stress of loose mercerized yarns than the loose decrystallized.

Yarn strengths measured while in the solutions at normal rates of strain are decreased slightly by ethylamine, but are decreased appreciably by 19% NaOH solution. Both yarns and single fibers show an equilibrium condition at a low strain, below which stress increases and above which stress decreases, when fibers are swollen with 19% NaOH or ethylamine.

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Part II: Effects of Strains During Swelling, Washing, and Drying

Rollin S. Orr, Albert W. Burgis, Joseph J. Creely, Trinidad Mares, and James N. Grant

Abstract

Yarns from samples of Pima S-1 and Hopi Acala varieties were mercerized and decrystallized when strain was controlled to provide unrestricted shrinkage in length, normal length, and 3% extension beyond normal length during ethylamine treatment. Comparisons of effects of sodium hydroxide and ethylamine at different strain conditions were made from measurements on the cellulose, tensile properties of fiber bundles and yarns, and elastic behavior of the yarns. Densities of the mercerized are in general below those of the decrystallized if occluded solvents are removed. The lower densities are in accord with the higher moisture regains for mercerized than decrystallized cottons.

Strains had no influence on the crystallinity ratio during decrystallization but prevented complete conversion to cellulose type II in mercerization. The decreases in bundle tenacities with increases in gauge length were essentially equal in the decrystallized and untreated cottons but smaller in the mercerized. Yarn tenacities of the mercerized and untreated increased as the moisture regain was increased, while those of the decrystallized were essentially equal at standard and wet conditions. Elongation at break was decreased by strain during treatment and increased with moisture in the sample when tested. The slack mercerized or decrystallized yarns when strained to

less than 2% of their elongation at break have greater recovery and less permanent set than the untreated. At high strains or stresses the reverse in recovery and permanent set was found. Yarns treated at normal length have no appreciable difference in recovery and permanent set from that of the untreated.

Introduction

The effects of anhydrous ethylamine and sodium hydroxide as swelling agents on physical properties of cotton fibers and yarns when free to contract in length during swelling were discussed in Part I [9]. A restriction in the swelling forces and alignment of fibers through strains on yarns during mercerization is known to alter strength and elongation of both fibers and yarns [4]. Previous investigations have shown that cottons are unlike in some instances in their behavior during and after swelling with caustic [4, 7].

In the present investigation, the permanent effects on properties of fibers and yarns swollen with anhydrous ethylamine have been compared with those swollen with sodium hydroxide. Since the strains on yarns during swelling affect the chemical changes, accurate control was maintained in both the amounts of strain and the stages of application to provide materials with ranges in strain histories. Also, yarns from two cottons which have shown differences in their response to treatments were swollen under identical strains. In addition to the tensile and elastic properties, the changes in cellulosic structure caused by the treatments were investigated for each of the cottons given the different treatments.

Experimental

Samples

Yarns used in the studies, processed from cottons of Hopi Acala and Pima S-1 varieties, were described in an earlier publication [9]. While changes in properties were measured principally from fiber bundles and yarns of 36.9 × 2 tex (16/2) construction with low twist (12 turns/in. singles), the effects of twist were measured on yarns of Pima S-1 of 42.1 × 3 tex (14/3) construction with both low (11.2 turns/in. singles) and medium twists (15.3 turns/in. singles). Twists in plies were balanced against those of the singles to minimize twist changes during treatment or testing.

Apparatus

A cross-sectional view of the frame and chamber used to mercerize or decrystallize the yarns at desired strains is given in Figure 1. Yarns as skeins were treated while looped over spools on spiders A and B. Strains on the skeins were established by the distance between the spiders and were changed as desired by the telescoping construction of the frame and the threaded screw C. Temperature of liquids in the cylinder was controlled as desired by passing cold water or steam through the copper coils E encircling the glass cylinder.

Treatment

The procedures during treatment with the swelling agents differ from those practical for commercial processes, but special conditions were necessary to minimize differences in swelling and chemical changes when investigating the effects of strains.

Six skeins of yarns from each of the untreated cottons were placed over the spools on the frame and the unit lowered into the glass cylinder. After the top was covered, the glass cylinder was filled with a decrystallizing liquid, anhydrous ethylamine, at a temperature between 0° and 10° C. At the end of 4 hr. of treatment the cylinder was drained and filled with chloroform and heated to a temperature near 60° C. The hot chloroform was replaced with chloroform at room temperature and the yarns permitted to soak for 3 hr. A third change of chloroform at room temperature was left in the cylinder for 16 hr. Small swatches of the yarns were removed for testing; soaking was continued if necessary until ethylamine content was less than 1%.

Yarns were treated also in mercerizing solution consisting of 20% by weight sodium hydroxide and 0.5% wetting agent at a temperature of 20° C. They were immersed in the caustic for 20 min. and then washed with water. After the first wash, the alkali in the yarns was neutralized with 0.5% solution of acetic acid and the yarns given additional washes with four exchanges of water. The combined washing and soaking periods for mercerization extended

over a period of 20 hr. to insure complete removal of reagent.

The identical strain conditions in the decrystallization and mercerization treatments consisted of yarns completely relaxed, yarns relaxed during swelling but strained to normal length prior to drying, and yarns strained to normal length throughout the treatment. Additional decrystallization treatments included yarns swollen while relaxed and strained to greater than normal length during washing and drying and yarns strained to less than normal length both before and after the chloroform extraction.

Test Methods

The procedures used to measure the physical properties of untreated and treated yarns followed in general those described in the literature [1, 2]. The following cellulosic changes were measured according to methods described: crystallinity index [11, 12], leveling-off degree of polymerization (LODP) [6], and density [8]. A slight modification in method of preparing samples for density measurements included the drying of samples over silica gel followed by a 5-min. boil in carbon tetrachloride.

Moisture regain, linear density, and tensile-elastic properties were measured after yarns had been conditioned for 7 days at 70° F., 65% RH.

The tensile-elastic properties were measured with the TRI-Schaevitz electronic [1] tester [10] at extension rates which caused the yarn to break in 0.5–1.0 min. Breaking strength and elongation were measured also on the wet yarns, which were soaked in distilled water for 1 hr. before testing. Tensile properties were obtained on yarns which had been dried by a desiccant and tested in a chamber of air at 10% RH.

Elastic recovery properties were measured by a modification of the technique described by Susich and Backer [13]. All strains were measured from the length of the yarn under a 20-g. load. The rate of strain was changed to give approximately equal time to break for yarns of each treatment. Immediate recovery is the observed strain recovered as measured from the curves without correction for recorder response. Complete diagrams of the immediate recovery (IR), delayed recovery (DR), and permanent set (PS) were prepared from load recovery curves for a minimum of five progressively increased intervals between zero and break. The period of relaxation of 1 hr. was allowed between cycles for delayed recovery and permanent set.

[1] Use of a company and/or product named by the Department does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

Results and Discussion

The measurements for physical properties of two cottons (Pima S-1 and Hopi Acala) given in Part I [9] and of several cottons in other investigations [3] have shown that differences exist in response of cottons when given a chemical treatment under identical conditions. Since the Pima S-1 and Hopi Acala usually reflected the maximum and minimum changes depending upon the property or properties considered, data to be reported in Part II will be confined to values for these cottons as typical of extreme changes to be encountered in American cottons.

In Table I are given the values for the structural and cellulosic properties of the untreated, scoured, chloroform extracted, and for the decrystallized and the mercerized cottons at several strains during the treatment.

The weight losses on heat drying (moisture regain) [2] and the changes in weight with treatment are within the range expected for untreated, scoured, and mercerized yarns. However, weight losses on oven drying of the decrystallized are slightly larger

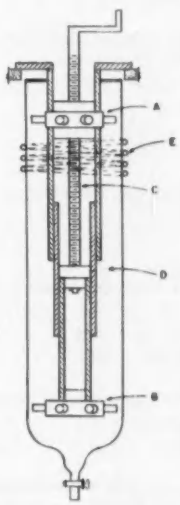

Fig. 1. Sketch of rack and chamber for chemically treating yarns at specified strains.

TABLE I. Properties of Cotton Before and After Decrystallization and Mercerization Treatments

Sample identification	Density, g./cc.	Moisture regain,† %	X-ray crystallinity index‡		LODP	
Untreated						
Pima S-1	1.547	6.8	77	±5	220	±10
Hopi Acala	1.551	6.7	83	±5	228	±10
Scoured						
Pima S-1	1.548	7.3			228	
Hopi Acala	1.550	7.2			228	
Chloroform extracted						
Pima S-1	1.548	6.8			218	
Hopi Acala	1.550	6.6			225	
Decrystallization						
D-1: Swollen, chloroform extracted, and dried without tension						
Pima S-1	1.511*	9.2	28		137	
Hopi Acala	1.513*	9.2	47		136	
D-2: Swollen without tension; chloroform extracted and dried at normal length						
Pima S-1	1.524*	8.0	22		115	
Hopi Acala	1.529*	7.6	19		129	
D-3: Swollen, chloroform extracted, and dried at normal length						
Pima S-1	1.530*	9.7	27		130	
Hopi Acala	1.537*	10.9	29		143	
D-4: Swollen without tension; chloroform extracted and dried at 3% extension						
Pima S-1	1.523*	8.3	25			
Hopi Acala	1.518*	8.3	22			
Mercerization						
M-1: Swollen, washed, and dried without tension						
Pima S-1	1.524	10.8			149	
Hopi Acala	1.528	10.8			134	
M-2: Swollen without tension, washed, and dried at normal length						
Pima S-1	1.522	10.4			144	
Hopi Acala	1.530	10.5			144	
M-3: Swollen, washed, and dried at normal length						
Pima S-1	1.527	10.4			150	
Hopi Acala	1.531	10.5			139	

* Densities after removal of chemicals 1.535–1.539 g./cc.; error, ±0.001.

† Weight loss on oven drying [2].

‡ Method not applicable to mercerized fibers.

than moisture regain values of 7.2–8.0% given in an earlier report [3].

The decrystallized yarns after treatment were found to have increased in weight ranging from 8.7% to 12.6%, the increases inversely related to the densities (Table I). A discoloration of white paper used to protect these decrystallized yarns and the gains in skein weight were evidence that one or more of the treating chemicals had not been removed. Also, odors of chloroform and ethylamine were found in stored yarns and in those placed in a sodium hydroxide solution.

The occluded chloroform and ethylamine (apparently entrapped in the fibers) were removed from yarns by swelling with water and drying in xylene and carbon tetrachloride [8]. Losses in weight equal to 70% of the gains for yarns and increases in densities to values within a narrow range, 1.535–1.539 g./cc., with no apparent difference between treatments at different strains were observed.

The densities of the mercerized samples were slightly below those reported (1.518 and 1.533 g./cc.) for slack and normal length mercerization respectively [4]. Fibers swollen without tension had densities lower than those mercerized at normal length. The procedure for removing occluded solvents from the decrystallized when applied to scoured or to mercerized cottons had no effect on the densities. With decrystallization at normal length as an exception, the Hopi Acala samples had densities greater than the Pima S-1 samples, both as untreated cotton and after the different treatments.

The crystallinity indices as measured from radial tracings of x-ray powder patterns [11, 12] were reduced by the ethylamine treatments from 77% and 83% for Pima S-1 and Hopi Acala respectively to values ranging from 19% to 47%. No simple relationship between the crystallinities and the strains during treatment was found. The method of measuring crystallinity for the decrystallized was not applicable to mercerized cotton. However, essentially complete conversion to the cellulose II crystal lattice was found in yarns mercerized without tension, but mixtures of celluloses I and II were found in yarns swollen at normal length. These observations are consistent with the lower density of yarns with complete conversion to cellulose II.

A significant reduction in leveling-off degree of polymerization (LODP), slightly greater in decrystallization than in mercerization, was observed

with both types of swelling treatments. Differences in LODP which could be related to the strains during treatment were not evident from the measurements.

Both the density (after deocclusion) and moisture regains indicated that the mercerized samples had lower crystallinity values than the decrystallized samples. However, the LODP values indicated a lower crystallinity in the decrystallized samples (Table I). Since neither measures are considered as absolute values for the amounts of crystalline cellulose present in a sample, the inconsistencies for these treatments may be attributed to differences in sizes of the crystallites and to the relative amounts of mesomorphic cellulose present after treatment.

Bundle Tenacity and Elongation at Break

In Table II are given the bundle tenacities and elongations at break for fibers from the treated yarns. The tenacity and elongation at break for $\frac{1}{8}$-in. gauge length was used to calculate the modulus and toughness index. Since the decrease in tenacity with increase in gauge length has been attributed in part to

TABLE II. Bundle Tenacities and Elongations of Fibers from Untreated and Treated Yarns

Sample identification	Tenacity 0 in., g./tex	Tenacity $\frac{1}{8}$ in., g./tex	Decrease 0–$\frac{1}{8}$ in., %	Elongation $\frac{1}{8}$ in., %	Modulus* $\frac{1}{8}$ in., g./tex	Toughness† index $\frac{1}{8}$ in., g./tex
Untreated						
Pima S-1	39.7	27.7	29	9.6	290	1.33
Hopi Acala	39.0	22.0	44	6.8	380	0.75
Scoured						
Pima S-1	39.0	28.1	28	10.4	270	1.46
Hopi Acala	38.2	22.2	42	7.6	292	0.84
Chloroform extracted						
Pima S-1	41.5	29.2	30	10.2	287	1.49
Hopi Acala	43.7	22.4	49	6.2	360	0.69
Decrystallization						
D-1: Swollen, chloroform extracted, and dried without tension						
Pima S-1	37.2	26.6	28	11.5	231	1.53
Hopi Acala	38.7	22.8	41	8.1	282	0.92
D-2: Swollen without tension; chloroform extracted and dried at normal length						
Pima S-1	36.1	28.3	22	8.5	333	1.20
Hopi Acala	42.0	24.4	42	6.0	407	0.73
D-3: Swollen, chloroform extracted, and dried at normal length						
Pima S-1	39.5	27.6	30	10.0	276	1.38
Hopi Acala	41.6	23.6	43	6.8	408	0.64
Mercerization						
M-1: Swollen, washed, and dried without tension						
Pima S-1	30.2	26.6	12	23.9	111	3.18
Hopi Acala	31.9	25.5	20	16.8	157	2.08
M-2: Swollen without tension; washed and dried at normal length						
Pima S-1	36.7	32.1	12	8.3	387	1.33
Hopi Acala	37.9	29.6	22	5.9	500	0.88
M-3: Swollen, washed, and dried at normal length						
Pima S-1	36.5	29.6	19	8.8	337	1.31
Hopi Acala	39.0	26.8	31	6.5	412	0.87

* Tenacity (g./tex)/elongation at break (%).
† Tenacity (g./tex) × elongation at break (%)/2.

the presence of weak points along the fiber [14], the percentage decrease in tenacity is considered a measure of strength uniformity along the fiber length. In the untreated cotton the percentage decrease is greater for the Hopi Acala than for the Pima S-1.

The processes of scouring, chloroform extracting, and decrystallizing produced no great changes in tenacity or the measure of strength uniformity as defined above. In contrast, mercerization generally produced decreases in tenacity at zero gauge length (greater decreases occurring for slack treated) and increases in tenacity at $\frac{1}{8}$-in. gauge length (greater increases occurring in samples swollen without tension, washed, and dried at normal length). These decreases at zero gauge length and increases at $\frac{1}{8}$-in. gauge length resulted in an increase in the measure of strength uniformity for mercerized yarns. The increases at the longer gauge length could be attributed, for mercerization under strain, to a better alignment of the elements of the fibers from wet stretching. Similar effects were not observed in the decrystallized samples which were stretched while wet with chloroform.

The elongation at break was increased by slack

TABLE III. Effects of Moisture Conditions on Tenacity and Elongation of Yarns at 70° F.

Sample identification	Linear density, tex	Tenacity, g./tex			Elongation at break, %		
		10% RH	65% RH	Wet	10% RH	65% RH	Wet
Untreated							
Pima S-1	74.1	18.8	25.9	28.5	5.7	9.0	11.6
Hopi Acala	73.2	11.9	16.1	23.1	4.2	6.2	9.2
Scoured							
Pima S-1	70.5	20.6	26.1	27.4	7.3	9.7	11.3
Hopi Acala	72.2	13.3	18.0	21.8	5.4	7.3	8.8
Chloroform extracted							
Pima S-1	73.7		26.9			9.1	
Hopi Acala	73.8		21.1			7.2	
Decrystallization							
D-1: Swollen, chloroform extracted, and dried without tension							
Pima S-1	83.7	22.2	26.1	26.1	10.0	13.5	13.7
Hopi Acala	84.1	16.4	22.5	22.5	7.8	10.9	11.0
D-2: Swollen without tension; chloroform extracted and dried at normal length							
Pima S-1	78.0	24.7	27.7	27.3	7.0	9.2	10.9
Hopi Acala	79.4	20.7	24.4	24.4	5.6	7.5	8.9
D-3: Swollen, chloroform extracted, and dried at normal length							
Pima S-1	78.0	24.7	28.2	28.7	6.7	9.6	10.9
Hopi Acala	76.2	21.1	24.2	25.7	5.1	7.3	8.7
D-4: Swollen without tension; chloroform extracted and dried at 3% extension							
Pima S-1	74.6		30.6			7.2	
Hopi Acala	77.7		25.2			6.1	
Mercerization							
M-1: Swollen, washed, and dried without tension							
Pima S-1	89.0	21.0	25.2	23.9	19.2	24.7	23.4
Hopi Acala	87.2	17.5	21.2	21.8	13.8	18.7	19.8
M-2: Swollen without tension; washed and dried at normal length							
Pima S-1	74.4	29.7	28.8	31.0	5.1	5.9	9.1
Hopi Acala	75.4	25.3	23.1	26.5	4.0	4.4	7.0
M-3: Swollen, washed, and dried at normal length							
Pima S-1	74.0	26.5	28.2	30.7	5.4	7.2	9.3
Hopi Acala	71.5	20.8	22.8	26.8	4.4	5.5	7.6

treatment but in general was decreased when the yarns were treated under tension. Also, the elongation increases, which were larger in slack mercerization than slack decrystallization, must be attributed to differences in the types of swelling.

Tensile Properties of Yarns

The linear densities, tenacities, and elongations at break for the untreated and treated yarns are given in Table III. Tenacities at the three conditions, 10% RH, 65% RH, and wet, were calculated from their breaking loads at the test conditions and their linear densities at 70° F. and 65% RH. The linear densities from different treatments, however, reflect losses caused by removal of noncellulosic constituents, gains from occluded solvents and/or moisture, and the changes in length caused by differences in strain on the yarns during the treatments. When compared to the untreated, all treatments of both cottons showed increases in tenacity when tested at 10% RH. The Hopi Acala cotton consistently showed greater increases than Pima S-1. At 65% RH, there were smaller gains in tenacity of treated over the untreated, but the Hopi Acala maintained about the same increase over Pima S-1. At wet conditions, the gains and losses in tenacity were almost within experimental error. Increases in tenacities between 10% and 65% RH, evident in all of the samples, were greater than those between 65% RH and the wet conditions. Also, the increases were greater for the Hopi Acala than the Pima S-1 samples. The decrystallization of cotton caused no appreciable difference between the tenacities at wet and standard conditions. Only the untreated yarns and those mercerized and dried under strain had tenacities when wet greater than those at 65% RH.

The elongations at break increased consistently as the moisture in the yarns was increased. Differences in the tenacities of mercerized and of decrystallized cottons were not accompanied by similar differences in elongations at break. The effects of moisture on tenacities and elongations of both scoured and mercerized yarns discussed above are similar to those observed by Meredith [5].

Strain Recovery

In Figure 2 are plotted for yarns of Hopi Acala and Pima S-1 the strain and recovery properties for the untreated and seven treatments of each cotton. The area boundary curve for immediate recovery (IR) gives the percentages of the total strains placed on the yarns which is recovered in approximately 10 sec. during the removal of the applied load. The section of delayed recovery (DR) represents the percentages of the strains recovered during the period of 1 hr. relaxation, while the permanent set (PS) is the combined long period recoverable strain and permanent set.

The relationships between the recoveries and permanent set changes with strain applied and with the type of treatment. When yarns are strained to 2% or less of their length, the total percentages of recovery in both the decrystallized and mercerized is larger and permanent set smaller for slack treatments than for those with tension. Therefore, the permanent set at 2% strain is larger in those treated at normal length than those treated slack. In general for low strains, the delayed recoveries are larger percentages of the applied strain in the decrystallized than in the mercerized yarns.

Elastic recoveries at strains equal to 50% of their elongation at break or stresses of 50% of the breaking loads are appreciably different from those at the 2% strain. At higher strains or stresses, the permanent set is greater in slack treated than those treated under strain. The permanent set for slack treatments causes a significant increase in length which makes the length after high strains comparable to the original length of the yarn. Mechanical conditioning by straining or cyclic loading the yarn to a point near rupture also causes increases in length and decreases in permanent set. These changes are particularly large in slack mercerized and considerable in slack decrystallized samples; they occur to some extent in untreated samples. Subsequent wetting and drying these yarns while slack restores the untreated yarn to nearly its original length and permanent set, but only partially restores the slack mercerized or slack decrystallized yarns. Since yarns mercerized or decrystallized under a strain have a higher permanent set and a reduction in their elongation at break, the reduction in crystallinity appears to increase permanent set, particularly at high stresses.

Effects of Twist

The tensile and elastic behaviors were measured on untreated, boiled, chloroform extracted, and decrystallized yarns of low twist (11.2/7.9 turns/in.) and medium twist (15.3/10.8 turns/in.) in single and

plies respectively from Pima S-1 cotton. The untreated and decrystallized yarns both before and after boiling showed that elongations at break for the medium twist yarns were consistently greater than those of the low twists, even though the tenacities of the yarns were comparable. Elastic recovery measurements at 2% strain gave slight but consistently smaller percentages of permanent set and immediate recovery and larger percentages in delayed recovery in the medium than in the low twist yarns. Recoveries and permanent sets of the decrystallized yarns of the tex 42.1 × 3 (cotton 14/3) construction followed similar trends with respect to the untreated as those of tex 36.9 × 2 (cotton 16/2) given in Figure 2. At 50% of the elongation at break or 50% of the breaking load, the yarns of higher twist had lower percentages of immediate recovery and higher percentages of permanent set than those of the lower twist.

Summary

The densities of the decrystallized yarns as treated were lower than those of the mercerized. When occluded swelling agent was removed from the decrystallized samples, their densities were above those of mercerized samples. This is consistent with the lower moisture regain of the decrystallized cotton as compared to mercerized cotton. However, the lower LOPD and crystallinity of the decrystallized samples indicate complicated differences in fine structure.

Bundle tenacities are essentially unchanged by the decrystallization. However, slack mercerization decreased tenacities at the zero jaw spacing, while mercerization with a strain during swelling or drying

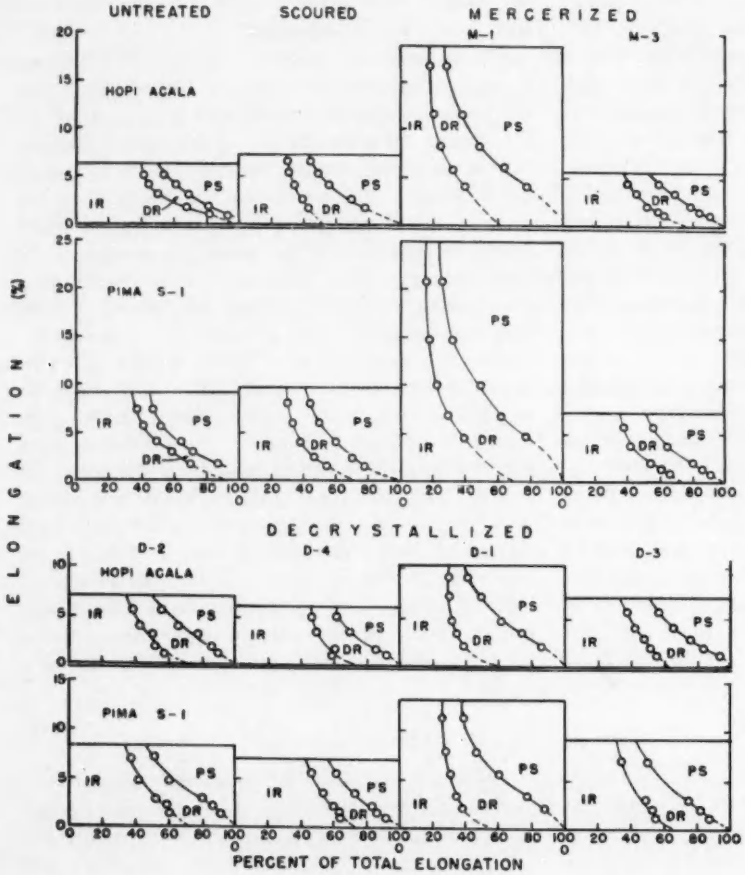

Fig. 2. Rectangular graphs showing immediate recovery (IR), delayed recovery (DR), and permanent set (PS) for untreated, scoured, mercerized (M), and decrystallized (D) yarns of Pima S-1 and Hopi Acala cottons. Yarn treatments: M-1 and D-1, slack; M-3 and D-3, normal length; and D-2 and D-4, slack when swollen but strained during chloroform extraction, D-2 to normal and D-4 to 3% above normal length.

increased tenacities at the $\frac{1}{8}$-in. spacing. Strength uniformity along the fiber length appears to be increased by mercerization but unchanged by decrystallization. Strain applied throughout mercerization was less effective than slack mercerization in increasing strength uniformity.

Yarn tenacities at standard conditions were increased by both decrystallization and mercerization when strain was applied during the treatment. These increases were greater in the Hopi Acala than the Pima S-1 and greater at 10% RH than at standard conditions. Tenacities of all decrystallized yarns and those slack mercerized were essentially equal at the wet and standard conditions. The untreated, scoured, and yarns mercerized under strain had wet strengths slightly above those at standard conditions. Strains greater than those required for normal length increased the yarn strength of the decrystallized.

Elongation at break was decreased by the strains on the yarns during the treatment and increased when the moisture regains were increased by changes in the atmospheric conditions during the test. Strains had greater effects on yarn elongations of mercerized than on the decrystallized.

The slack mercerized and decrystallized yarns, when strained to 2% of their elongation at break, have greater percentages of the strain recovered and lower percentages of permanent set than those of the untreated yarns. When the fibers are strained to 50% of their elongation at break or 50% of their tenacity, the permanent set is greater and recoveries smaller than those of the untreated. Mercerization or decrystallization under strain to retain the normal length caused no appreciable changes from the untreated at any of the given strain conditions. When yarns are swollen without strain and the strain applied during washing or drying, the recoveries and permanent sets were comparable to those of yarns treated at normal length. Although the changes in elastic properties are closely related to the contraction in length of the fiber during swelling, the reduction in crystallinity apparently increases the permanent set when high strains or stresses are applied.

Differences between the samples of Hopi Acala and Pima S-1 as untreated cottons were generally maintained, particularly in strength, strength uniformity, elongation, and density. Their behavior in general characterizes the extremes in responses of cottons to chemical treatments.

Acknowledgments

The authors wish to express their appreciation to J. J. Brown for having the special yarns processed, to L. Loeb for assistance in equipment design and treating methodology, to J. R. Jung, Jr. for assembling the equipment, to S. P. Koltun for assistance with decrystallization of the yarns, and Mrs. Ruby H. Tsoi for assistance with the manuscript.

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Letters to the Editor

Short communications in the form of Letters to the Editor are intended to provide prompt publication of significant new research results and to permit an exchange of views on papers previously published in the JOURNAL. These communications are not submitted to formal review as are research papers, and the editors do not assume any share of the author's responsibility for the information given or the opinions expressed. When work previously published in the JOURNAL is the subject of critical comment, the authors of the original paper are given an opportunity to submit a reply, which will be published concurrently when possible.

Correspondence Regarding "Application of Infrared Absorption Spectroscopy to Investigations of Cotton and Modified Cottons, Part I"

Beaunit Mills, Inc.
450 Seventh Avenue
New York 1, N. Y.
October 17, 1958

To the Editor

TEXTILE RESEARCH JOURNAL

Dear Sir:

In Part I of the article "Application of Infrared Absorption Spectroscopy to Investigations of Cotton and Modified Cottons" (May 1958), Dr. O'Connor and his associates of the Southern Regional Research Laboratory presented thirteen spectra of various fibers and indicated their usefulness for identification and measuring relative proportions of components of textile fibers in blended fabrics. We are in full agreement that this is an excellent solution to the problems now besetting the analyst due to the large number of similar but yet significantly different man-made fibers available to the textile industry. We would like to point out, however, that the spectrum of a given trade-named product is not a fixed or immutable property, and that, for example, the spectrum presented for Orlon [1] represents continuous filament Orlon no longer in production and not the currently produced staple fiber. In addition, one spectrum is given for Acrilan; we have tested two Acrilans of different spectra. A task group has been set up under the auspices of the ASTM which hopes to prepare an authenticated series of spectra suitable for qualitative purposes.

The sample preparation method described in Dr. O'Connor's article is of good general application. It is possible, however, with most synthetics to obtain spectra more quickly and of improved quality by the use of films cast from suitable solvents. For example, Saran was shown as giving a relatively featureless spectrum characterized by a lack of any sharp bands. A spectrum obtained from a Saran film cast from dioxane presents a different and much more specific picture. It should also be noted that films of the various synthetic fibers cast from or washed with different solvents present significantly different spectra which are, however, still characteristic of the fiber in question.

M. P. Bouriot of the Chemical Laboratory of the Textile Institute of France showed spectra of films cast from formic acid of nylon 66, nylon 6 (Perlon), and nylon 11 (Rilsan) at the time of the 29th Congress of Industrial Chemistry in Paris, November 1956, in which he indicated that these three fibers could be separately identified without ambiguity by reference to their IR spectra.

BRAHAM NORWICK

[1] Du Pont trademark.

Reply to Norwick Letter

Southern Regional Research Laboratory [1]
New Orleans, Louisiana
November 13, 1958

To the Editor

Textile Research Journal

Dear Sir:

The thirteen spectra presented in our paper "Applications of Infrared Absorption Spectroscopy to Investigations of Cotton and Modified Cottons, Part I" were intended merely to illustrate how KBr disc spectra could be used to differentiate various synthetic and natural fibers. The primary purpose of this paper was to report on the applicability of this technique to modified cottons. It was not intended to be an exhaustive investigation of the various types of all the different synthetic fibers.

We cannot agree with Dr. Norwick that spectra obtained from cast films are of improved quality compared to KBr disc spectra, nor that they can be obtained more quickly. We prefer KBr disc spectra for the following reasons. (a) The spectra are obtained without modification of the fiber. Thus, we are able to follow the decrease in crystallinity of cotton, e.g., on grinding in a vibratory type mill or when treated with ethylamine, and obtain results which correlate very well with those from x-ray diffraction methods. With spectra from cast films, such studies would be meaningless, as in preparing the cast film the fiber would be thoroughly decrystallized. (b) KBr disc spectra can be made quantitative with no difficulty or increase in time. This is illustrated, particularly, in Part II of our contribution, with the quantitative analysis of extent of acetylation or cyanoethylation of cotton. Spectra from cast films cannot be made quantitative, except by introduction of some "internal standard." The thickness of these films cannot be reproduced from time to time and will vary for different positions of a given film. Thus, quoting from our paper (Reference 3), Brown et al. recommend, for example, the lengthy procedure of "measuring such films at several positions and using average readings to overcome lack of homogeneity." Such a technique is not appealing as a rapid method of obtaining satisfactory spectra. (c) While suitable cast films can be obtained readily from several synthetic fibers, these types of films either cannot be obtained or when obtained are very unsatisfactory in the case of modified cottons.

As Dr. Norwick points out, various synthetic fibers cast from different solvents will present significantly different spectra. However, this is not a particularly critical problem, for exactly the same situation occurs in solution spectra, where the spectra will vary, sometimes considerably, from solvent to solvent. Comparisons, of course, will have to be limited to spectra obtained from films cast from the same solvent.

We heartily approve the establishment, under the auspices of the American Society for Testing Materials, of a Task Group in Commitee B-1 on "The Identification of Fibers." We expect to work with Dr. Norwick on this Task Group and believe the data obtained will be of considerable value to all segments of the textile industry. We feel, however, that except in isolated cases where the cast films technique is particularly satisfactory, KBr discs will produce better quality spectra.

Robert T. O'Connor
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Electron Microscope Observations on Helical Structure in Starch

Clemson College
Clemson, S. C.
December 19, 1958

To the Editor

TEXTILE RESEARCH JOURNAL

Dear Sir:

After the discovery of the helical structure of many polypeptides and protein molecules, it has become more and more evident that such structures constitute a principle of wide significance, not only on the molecular level, but also on a higher level as "super" helical structures. For natural polymers, Pauling and Corey [10] and Crick [2] pointed out the existence of helices twisted about one another to form more complex structures, and Pauling [9] has given a general discussion of helical aggregation of gobular proteins. The helical arrangement of subunits in tobacco mosaic virus [19] is another example of superhelical structure.

In spherulites of synthetic polymers, Keller [6] demonstrated the existence of helical crystalline aggregates and Morgan [8] discussed coiling crystal growth as a general principle in the crystallization of synthetic polymers. According to the latter author, lateral accretion of polymer molecules to the already existing helical crystals could lead to branched growth and the formation of coiled families of fibrillar crystals in synthetic polymers.

In an electron microscope study of soluble starch, the author made observations which are entirely in line with the above ideas. Some of the results are presented in Figures 1–4. These are electron micrographs obtained from a solution of soluble starch dissolved at about 70° C. and sprayed and shadow casted with platinum following conventional methods. The pictures are shown at 10,000 × magnification at progressive stages of disintegration of the starch particles. They show typical helical configurations, which are still closely packed together in Figure 1 but are increasingly separated in Figures 2 and 3.

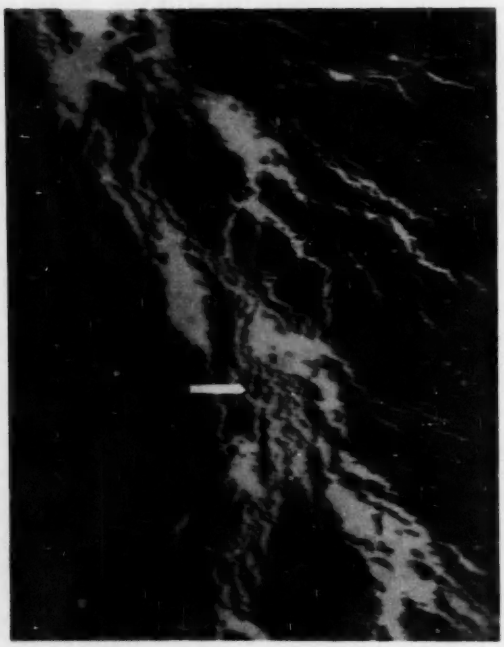

Fig. 1. Electron micrograph of soluble starch particle showing a composite of helical structures; 10,000 ×.

Fig. 2. Same as Figure 1, showing increased separation of helices and also scattered spherical bodies; 10,000 ×.

The diameter of the single helices varies from about 100–500 Å. This dimension and its variability suggest that the helical structures are not identical with single molecular helices (which have a diameter of about 13 Å; see below), but are, at least for the greater part, *super*-helical (probably microcrystalline) structures, consisting of more than one molecule. The pitch of the helices is also variable. In Figure 4, of a less disintegrated particle, it seems to be less than 45°, but in Figure 1 the pitch is often more than 45°. Branching of the helical structures is sometimes seen, especially when the particle is less disintegrated (Figure 4).

The above observations suggest that in the starch grain the macromolecules of starch form long coiled polymer crystals or aggregates extending in radial direction of the grain in the same way as postulated for spherulites of synthetic polymers.

These findings with the electron microscope may be of interest in connection with conclusions obtained by other methods on the helical configuration of the starch molecule. A helical configuration of the starch–iodine complex in solution was proposed around 1940 by Hanes [5], Freudenberg et al. [3], and Caesar and Cushing [1] and has been concluded from physical chemical studies by Rundle and coworkers [15]. This helix would contain six glucose residues per turn, forming an angle larger than 45° with the axis. By x-ray investigations Rundle and coworkers [16] confirmed this conclusion and showed that the helical configuration also occurs in the V modification of starch [14] and in less perfect, crumpled form also in certain starch fibers [12]. The diameter of the helix was found to be 13.7 Å. In the α and β modification, however, the starch chain molecule would occur in the fully extended form [11, 13]. From x-ray diffraction studies of various amylose compounds, Senti and Witnauer [17] concluded that the amylose chain possesses here fourfold screw symmetry with four glucose residues corresponding to the fiber repeat period. On the basis of x-ray studies of part of a single starch grain, Kreger [7] concluded that the α and β modification of (native) starch would also have helical configuration, but he accepts a more extended helix (chain axis forming an angle less than 45° with the axis of helix) with three glucose residues per turn (threefold screw axis).

The super helical structure observed here with the electron microscope may be also of interest for certain problems [4] regarding the orientation of the refractive index ellipsoid in native starch.

On the side of the helical structures observed, most preparations also contain spherical particles. These are clearly seen in Figure 2; their diameter is about 500–2000 Å. They might correspond to the globular molecules or molecular aggregates, studied by Stacy and Foster [18]. These authors found that in a solution of corn amylopectin, molecular (or nearly

Fig. 3. Same as Figure 1, showing further separation of helices; 10,000 ×.

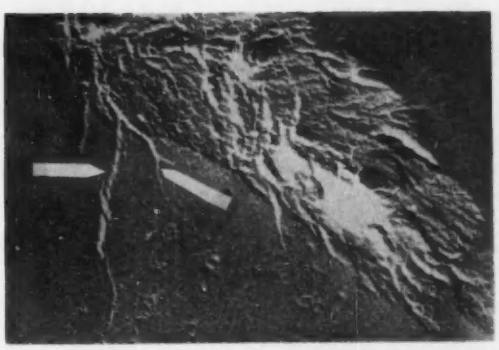

Fig. 4. Same as Figure 1. Dense particle showing branching of helix at its side; 10,000 ×.

molecular) particles occur with a radius of gyration of about 1500 Å, a spherically symmetrical distribution of matter, and a molecular weight of 80 million. Both random coils and (super) helices would then occur side by side in the starch solution investigated here.

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A. N. J. HEYN

Effect of NaOH on BX Rayon Yarn

Central Research Laboratories
Toyo Rayon Co. Ltd.
Otsu, Japan
October 28, 1958

To the Editor

TEXTILE RESEARCH JOURNAL

Dear Sir:

Hermans and his coworkers [3, 4] measured the crystallinity of cellulose rayons with a standardized x-ray method after previous treatment with 18% NaOH. Roseveare [6] examined the action of NaOH on several types of cellulose rayons by determining the amount of hydrolytically reactive material. Based on the data obtained from these investigations, rather well established opinion is that the effect of aqueous alkali treatment on the regenerated cellulose structure is usually the increase of both the crystallinity and the crystal size, just the opposite of that observed for native cellulose. As the cellulose chains gain an increased mobility by swelling, they will tend to relieve their high local strains resulting from the rapid precipitation in the spinning bath and to readjust to a more stable ordered configuration. Thus the crystal growth as well as the crystallinity increase occurs at the expense of low-ordered regions, probably in much the same manner as does the recrystallization on relief of strain by chain cleavage in hydrolytic media [5]. It is obvious that the magnitude and character of the changes caused by alkali swelling cycle are closely dependent upon the structure existing originally in each type of regenerated cellulose fiber.

Recently in our laboratory marked changes in hydrocellulose have been revealed by electron microscopy as a result of aqueous alkali treatment of BX yarn. This is a novelty kind of viscose rayon, produced in France by high concentration sulfuric acid spinning similar to the old Lilienfeld process [2]. Electron microscopical examination of the mixer ground preparations has shown a highly developed microfibrillar structure, as represented in Figure 1.

A specimen of BX yarn, after being extracted with ethanol benzene mixture, was soaked in aqueous

NaOH of varying concentration at 25° C. for 1.5 hr., then washed thoroughly with distilled water and dried. For acid hydrolysis 2.5 *N* HCl was used at 105° C. for 30 min. [1]. Hydrolysis residues were recovered on a No. 4 glass filter, then washed and dried.

The electron micrographs of the hydrocelluloses, prepared by ultrasonic dispersion, demonstrate clearly the changes produced by the alkali swelling cycle involved, as shown in Figure 2. Of course, the hydrolysis residues are not resolved into discrete particles, but are observed only in an aggregated form, so that no attempt has been made to determine the length of the individual crystallites. However, it would be quite probable that the changes revealed there are due to the changes in the shape and size of the crystallites themselves. This postulate would be supported by the measurement data of the leveling-off D. P., which are listed in Table I.

With increase in NaOH concentration up to 15%, the amount of material dissolved increases, while the loss in weight during the subsequent hydrolysis de-

TABLE I

NaOH concentration, %	0	5	8	10	12	15
Weight loss, %*						
During swelling cycle	0	0.7	4.7	4.3	6.4	7.8
During acid hydrolysis	18.8	15.4	14.1	11.9	13.0	8.8
Total	18.8	16.1	18.8	16.2	19.4	16.6
D. P.†						
After swelling cycle	630	—	—	—	—	640
After acid hydrolysis	46	50	60	66	69	72

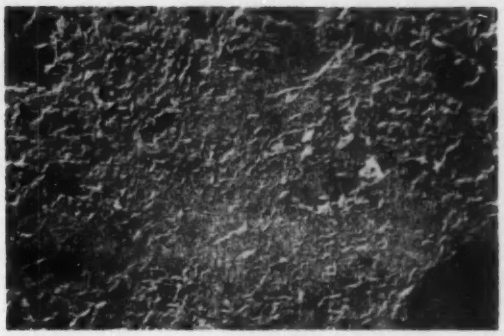
* The percentages of weight loss were represented with respect to the original cellulose on dry basis.

† The intrinsic viscosity was determined in cuprammonium solution (100 mg. of sample dissolved in 20 cc.). D. P. was calculated as follows:

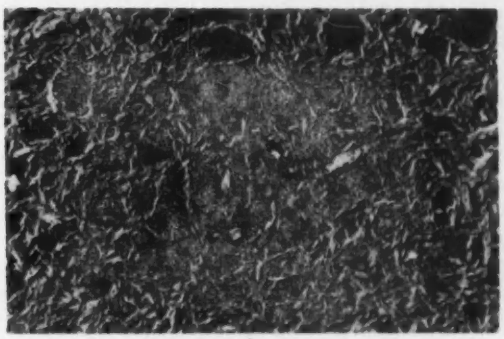
$$[\eta] = \frac{\eta_{sp}/C}{1 + 0.28\,\eta_{sp}}, \quad \text{D. P.} = \frac{[\eta]}{Km}$$

where Km equals 5×10^{-4}.

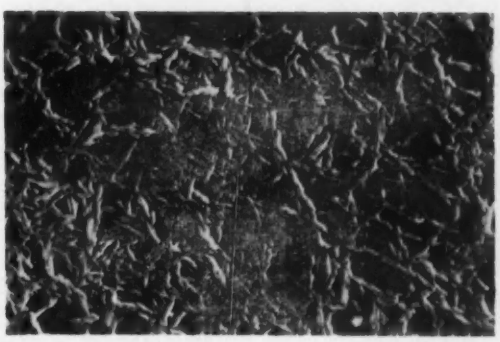
Fig. 1. Electron micrograph of BX yarn ground by mixer in water. In order to give more details the fiber specimen was previously stained by a kind of silver reagent. Cr shadowing (3:1); 17,000 ×.



a



b



c

Fig. 2. Electron micrographs of hydrolysis crystallites of BX yarn dispersed by ultrasonic vibration. (a) Untreated sample (D.P. 46). (b) Treated with 10% NaOH (D.P. 66). (c) Treated with 15% NaOH (D.P. 72). Cr shadowing (3:1); 20,000 ×.

creases. Consequently, the total losses are found to be approximately constant over the range of NaOH concentration tested. This fact suggests that the fraction to be lost by the acid hydrolysis applied here might be predetermined for the fiber specimen and that only a portion of the reactive fraction be dissolved away during the preceding alkali treatment.

In spite of the considerable weight loss and the serious change in appearance, the fiber retains its average D. P. almost unaltered after the swelling cycle. It appears that only some structural changes of a physical nature take place during the treatment.

The increase in the leveling-off D. P., on the other hand, is so pronounced as to reach finally 1½ times the original value. Of course, the technique used for determination of D. P. is rather approximate, but the increasing tendency would be too evident to be overlooked. In addition, as noted above, this increasing changes in the leveling-off D. P. are correlating quite well to the changes in the hydrocelluloses revealed under electron microscope.

From the experimental results presented above, one might reason that the submicroscopic structure of BX yarn is composed of a series of ordered regions as follows.

1. Regions of the lowest order, dissolved in aqueous alkali without any cleavage of molecule chains, perhaps playing a largely decisive role for a number of properties of practical importance, such as water imbibition, shrinkage, dyeing, etc.

2. Regions of the second lowest order, dissolved not in aqueous alkali, but in the hydrolyzing acid as a result of the chain cleavage.

(These two regions are considered to be present as interfibrillar, rapidly reactive material in a roughly predetermined amount.)

3. Regions of so low an order as to be subjected to hydrolytic splitting, but simultaneously rearranged into the crystalline residue, just due to the chain cleavage involved. Therefore, they can be responsible for the decrease in D. P. but not for the loss in weight, at least during the early period of hydrolysis.

4. Regions of order similar to 3, except that they become insensitive to the hydrolytic attack by the action of aqueous alkali. If such a region were between two regions of higher order, an alkali swelling cycle would give rise to their joining end to end or side by side.

5. Regions of order high enough to be resistant against the hydrolyzing agent, but not of perfect order.

(These three regions are considered to be present as intrafibrillar or intercrystalline amorphous material, probably responsible for the excessively higher estimate of crystallinity obtained by the hydrolytic method than those by other physical methods, such as x-ray and moisture sorption.)

6. Regions of the highest crystalline order.

It has been well proven that the hydrolysis crystallite is a product of recrystallization, which would be particularly intense for regenerated cellulose rayons. Therefore, slight crystal growth or rearrangement, even if it occurred, could not be detected by the examination of hydrolytic residues. In order to give a reasonable interpretation for the remarkable change in the hydrocellulose of BX yarn demonstrated here, it might be necessary to consider not only simple elongation of individual crystalline regions, but also longitudinal joining of adjacent crystallites through a mechanism such as noted above.

Whether or not the picture depicted for only one specific type can be generalized to other various types of regenerated cellulose fibers must be decided by more extensive investigations. Further work is in progress.

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KOICHI KATO
KOICHI YAMADA

Book Review

Identification of Textile Materials, Fourth Edition, Manchester, The Textile Institute, 1958. 148 pages.

Reviewed by M. L. Staples, Ontario Research Foundation, Toronto, Ontario, Canada

The rate at which new fibers have appeared on the market during the past few years makes frequent revisions of a work of this kind necessary. This is the fourth and greatly enlarged edition since Technical Committee "C" of the Textile Institute first published the "Identification of Textile Materials" almost 20 years ago. Many improvements have been introduced into the present edition to meet the changing needs of the textile analyst, and the scheme of analysis has been completely redesigned to deal with new fibers, finishes, and blends of fibers.

The first section of the book on the properties of textile fibers has been rewritten and presents information on over 40 different animal, vegetable, mineral, and man-made fibers. Additional information, frequently useful in fiber identification, is contained in tables of data on the densities, refractive indices, contraction, and softening temperatures of various fibers.

The two analytical schemes for identifying fibers which the book describes require the use of a microscope and other equipment generally found in a textile laboratory. In the first scheme, microscopic examination is used to establish that only one type of fiber is present in the specimen. A flame test is then employed to sort the fibers into two groups—those which are thermoplastic and those nonthermoplastic at low temperatures. Further differentiation of the thermoplastic group is based on determinations of whether or not the fibers contain nitrogen or chlorine, and various confirmatory tests are given to establish the identity of the type of fiber.

The nonthermoplastic group is classified into subgroups—protein, cellulose, etc., depending upon whether the fibers do or do not burn, the nature of the residue, and the odor of the vapor produced when the fibers are exposed to a flame. Microscopic examination of longitudinal and cross-sectional views is recommended for differentiating among protein fibers; confirmatory tests depend upon the solubility of the fiber in specified solvents. A similar type of procedure is used to distinguish among the various cellulosic fibers. The noncombustible fibers, asbestos and glass, are identified microscopically.

The second analytical scheme is based upon fiber solubility alone. The fibers are sorted into one or other of five groups depending upon their solubilities in the solvents specified. The fibers within each group are distinguished by determining their behavior in various other solvents.

A section on fiber blends provides for the use of selected solvents to separate the fibers into groups and, where further identification is required within a group, either microscopic examination or solubility tests are used.

Procedures are described for stripping dyes and removing sizes, resins, and certain other finishes from textile materials which may interfere with fiber identification. The book contains 123 excellent photomicrographs showing longitudinal and cross-sectional views of 45 different fibers. A complete index provides ready reference to the methods available for identifying each particular type of fiber.

The analytical schemes presented contain methods for identifying practically all of the kinds of textile fibers that were of commercial interest in the United States at the time of its publication. The book will serve as a valuable source of useful information to all who are concerned with the analysis of textile materials.

Gordon Research Conference

July 13-17, 1959

The Gordon Research Conference on Textiles for 1959 will be held July 13–17 at Colby Junior College, New London, New Hampshire.

Individuals interested in attending are requested to send their applications to the Director. All applications must be submitted on the standard application form which may be obtained by writing to the office of the Director. Each applicant must state the institution or company with which he is connected and the type of work in which he is most interested. Attendance is limited to 100.

Requests for attendance at the Conference, or for any additional information, should be addressed to W. George Parks, Director, Department of Chemistry, University of Rhode Island, Kingston, Rhode Island. After June 15, mail should be addressed to Colby Junior College, New London, New Hampshire.

Textiles

Colby Junior College

New London, New Hampshire

Leonard Smith, *Chairman*

Fred Fortess, *Vice Chairman*

July 13

Harold P. Lundgren. New Findings in Wool Structure, Stability, and Modification.

Sheldon Sprague. The Relationship of Polymer Constitution and Fiber Fine Structure to Fiber Physical Properties.

July 14

V. W. Tripp and Fred Perkerson. Phenomena Associated with Cross-Linking of Cotton Cellulose.

Richard Steele and John L. Gardon. Chemical Control of Crease Recovery and Wash-Wear Effects in Cellulose Fibers.

July 15

E. L. Wittbecker. Interfacial Polycondensation.

E. E. Magat. Interfacial Spinning.

E. V. Martin. Kodel Polyester Fibers.

July 16

Joel Lindberg. The Measurement of Mechanical Properties and Prediction of Fabric Performance.

DeWitt R. Petterson and Stanley Backer. On the Mechanics of Nonwovens.

July 17

Jack C. Smith. Stress-Strain Relations in Yarns Subjected to High Speed Impact.